PB86-114725

Emission Assessment of Refuse-Derived Fuel Combustion: Suspension Firing

KVB, Inc., Irvine, CA

Prepared for

Environmental Protection Agency
Cincinnati, OH

Sep 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-114725

EPA/600/2-85/117
September 1985

EMISSION ASSESSMENT OF REFUSE-DERIVED FUEL COMBUSTION: SUSPENSION FIRING

by

J. K. Arand
L. J. Muzio
R. L. Barbour
KVB, Inc.
A Research-Cottrell Co.
Irvine, California 92714

Contract No. 68-03-2773

Project Officer

Michael Black

Alternate Technologies Division
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/2-85/117

2.

3. RECIPIENT'S ACCESSION NO.
PB86 114725/AS

4. TITLE AND SUBTITLE
EMISSION ASSESSMENT OF REFUSE-DERIVED FUEL COMBUSTION: SUSPENSION FIRING

5. REPORT DATE
September 1985

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J.K. Arand, L.J. Muzio, R.L. Barbour

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
KVB, Inc.
A Research-Cottrell Co.
18006 Sky Park Blvd.
Irvine, California 92714

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-03-2773

12. SPONSORING AGENCY NAME AND ADDRESS
Hazardous Waste Engineering Research Laboratory
Office of Research and Development
U.S. EPA
Cincinnati, OH 45268

13. TYPE OF REPORT AND PERIOD COVERED
Project Report 6/79-11/81

14. SPONSORING AGENCY CODE
EPA/600/12

15. SUPPLEMENTARY NOTES
Michael Black, P.O.; 513-684-7844

16. ABSTRACT

The suspension burning investigation was conducted in a horizontal laboratory boiler firing at a nominal heat input of 440 kw. The boiler had been modified to simulate large utility boilers and was further modified to investigate co-firing and tri-firing of coal, RDF, and hazardous liquids.

Criteria emissions were obtained for a large number of co-fired conditions; many showed reduced nitric oxide emissions with co-firing relative to coal combustion. Organic and inorganic samples of the flue gas showed only two conditions where polynuclear aromatic hydrocarbons (PAH's) were present. Those conditions were with tri-fired powder RDF, coal, and waste oil. Screening criteria showed levels of dioxins and polychlorinated biphenyls (PCB's) were below threshold values requiring complete analysis.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
168

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases ot toxic and hazardous substances to the environment also have important environmental and pubic health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small business in handling their wastes responsibly and economically.

The suspension burning investigation was conducted in a horizontal laboratory boiler firing at a nominal heat input of 440 KW. The boiler had been modified to simulate large utility boilers and was further modified to investigate co-firing and tri-firing of coal, refuse-derived fuel, and hazardous liquids.

The information contained herein will be of interest to those designers or users who are contemplating or working with a system similar to this co-firing system. Requests for further information regarding the production and utilization of refuse-derived fuel should be directed to the Thermal Destruction Branch, HWERL, Cincinnati.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

Ongoing efforts to identify acceptable means of recovering usable energy from municipal waste established the need for a program to investigate the potential emissions from three likely modes of combustion which could be used in refuse derived fuels (RDF) disposal. Laboratory-scale experimental programs were carried out to evaluate co-firing characteristics and emissions for RDF fuels using:

- grate (or bed) burning
- suspension burning
- fluidized bed burning

This report presents the results for suspension firing.

The suspension burning investigation was conducted in a horizontal laboratory boiler firing at a nominal heat input of 440 kW. The boiler had been modified to simulate large utility boilers and was further modified to investigate co-firing and tri-firing of coal, RDF, and hazardous liquids. During the study, the following parameters were investigated:

- RDF type
- RDF/coal ratio
- RDF/coal/hazardous waste ratio
- excess air
- staged combustion
- hazardous waste type

A powder type RDF was co-fired with coal at ratios up to 50 percent (heat input basis) and tri-fired with pulverized coal and hazardous liquid waste (40 percent/40 percent/20 percent, respectively on a heat input basis). A fluff type RDF was also co-fired with coal.

Criteria emissions were obtained for a large number of co-fired conditions; many showed reduced nitric oxide emissions with co-firing relative to coal combustion. Organic and inorganic samples of the flue gas showed only two conditions where polynuclear aromatic hydrocarbons (PAH's) were present. Those conditions were with tri-fired powder RDF, coal, and waste oil. Screening criteria showed levels of dioxins and polychlorinated biphenyls (PCB's) were below threshold values requiring complete analysis.

Suspension firing of the fluff type RDF was not satisfactory above 10 percent Btu basis due to incomplete combustion of the larger particles in the primary burner region of the laboratory apparatus.

CONTENTS

Section Page

SUMMARY & CONCLUSIONS S-1

1.0 INTRODUCTION 1

1.1 Background 3

1.2 Objectives and Approach 4

2.0 EXPERIMENTAL APPARATUS AND PROCEDURE 6

2.1 Combustion System 6

2.2 Burner Modifications 13

3.0 TEST MATRIX 23

3.1 Test Numbers 23

3.2 Test Fuels 23

4.0 EXPERIMENTAL RESULTS 28

4.1 Burner Configuration and Performance 28

4.2 Combustion Characteristics and Gaseous Emissions 28

4.3 Particulate Loading and Sizing 43

4.4 Trace Element 46

REFERENCES 64

APPENDICES:

A. DETAILED DESCRIPTION OF COAL FIRING EQUIPMENT A-1

B. SPECIAL SAMPLING METHODS B-1

C. BATTELLE REPORT C-1

ILLUSTRATIONS

Figure		Page
2-1	Schematic diagram of combustion facility	7
2-2	Coal feed schematic	8
2-3	Schematic of eighty-horsepower boiler	10
2-4	Powder RDF feed system	12
2-5	Fluff RDF feed system	14
2-6	Small-scale version of a full-size coal burner	15
2-7	RDF-coal burner schematic	17
2-8	Modified high volume sampling system	20
4-1	Nitric oxide emissions coal - single stage combustion	30
4-2	Sulfur oxide emissions - coal	31
4-3	Nitric oxide emission - coal - staged combustion	32
4-4	Effect of CEA RDF fraction on nitric oxide emissions. Single stage combustion	34
4-5	Effect of CEA RDF fraction on chlorine emissions	35
4-6	Chlorine emissions co-fired CEA RDF and coal. Single stage combustion	37
4-7	Effect of staged combustion on nitric oxide emissions. CEA RDF optimum fraction (50%)	38
4-8	Effect of Americology RDF fraction on nitric oxide emissions. Single stage combustion	39
4-9	Effect of staged combustion on nitric oxide emissions. Americology RDF optimum fraction (12%)	41
4-10	Typical particulate size distributions single stage combustion	45

TABLES

Table		Page
2-1	Gas analysis instrumentation	16
2-2	Trace element/organics analysis	19
3-1	Test matrix	24
3-2	AAS analysis for mercury, arsenic and antimony of fuel samples	26
3-3	Fuel analysis (as received)	27
4-1	Particulate loading and sizing summary	44
4-2	HVSS sample test points	47
4-3	List of HVSS samples selected for analysis and analyses performed	48
4-4	Liquid chromatography elution sequence	50
4-5	Distribution of compound classes in liquid chromatographic fractions of organic extracts	52
4-6	Organic composition determined by gravimetric and gas chromatographic analysis	53
4-7	Organic composition determined by gravimetric and gas chromatographic analyses on liquid chromatography fractions of combined washes and XAD-2 cartridges	54
4-8	Low resolution mass spectrometry results for selected liquid chromatography fractions	55
4-9	SSMS results for inorganic elements	57
4-10	AAS results for mercury	58
4-11	AAS analysis for mercury, arsenic, and antimony on second and third impinger solutions (combined)	59
4-12	Results of PAH spot tests on particulate filter extracts	60
4-13	PAH analysis of XAD-2 extracts of selected runs	62
4-14	Gas chromatography analysis for organic chlorine	63
4-15	Results of HRGC/HRMS analyses for 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin in XAD-2 extracts	63

SUMMARY & CONCLUSIONS

BACKGROUND AND OBJECTIVES

The incineration of municipal refuse or the use of landfills has in the past been a major avenue of disposal. Acceptable sanitary landfills are becoming more difficult to find and incinerators that meet new air pollution standards are very expensive. Typically, incinerators do not raise steam and all the heat generated is lost. However, there have been some attempts to utilize this source of heat by adding steam or hot water generation equipment to municipal incinerators. Since these heat recovery devices were typically an afterthought add-on, they were of low thermal efficiency when compared to utility or even industrial steam generation equipment.

Since utility boilers have the potential for accommodating the consumption of large amounts of municipal solid waste with efficient heat recovery, the feasibility studies on large utility boilers such as St. Louis/ Union Electric appeared to be well justified. Unfortunately, large commercial utilities, due to fuel cost pass-through provisions and contracted long-term fuel supplied, have very little economic incentive to pursue the use of refuse-derived fuel (RDF) as a power plant supplemental fuel. Based on FEA estimates, over 15 percent of all the energy consumed in the United States is utilized by industrial boilers to generate process steam. The total annual energy consumption by these boilers was in excess of 9,300 trillion kJ's. Therefore, it is appropriate to consider the industrial sector as a potentially higher user of municipal wastes as a supplemental fuel source.

The range of equipment used to combust fuels in either industrial or utility boilers is wide and the types of fuels are varied. The focus in this program was on coal firing using three current modes of combustion considered suitable for either sector. These modes are:

- Suspension Firing
- Overfired Stoker Combustion
- Fluidized Bed Combustion

The objective of the overall program was to obtain an emission assessment of these three modes of combustion when co-firing a base coal and refuse-derived fuels (RDF). This report addresses the evaluation of suspension fired emissions of co-fired coal and two types of RDF. Due to the increased interest in hazardous waste disposal, an assessment of co-fired or tri-fired coal/RDF/hazardous waste was also included in the program.

EXPERIMENTAL APPARATUS AND APPROACH

The experiments were conducted in a multifuel combustion facility capable of solids fuel firing rates to 880 kW. All of the experiments in this study were conducted at 440 kW. The basis of the combustion facility was a 780 kW firetube boiler which had been extensively modified to simulate utility boiler conditions. This included an indirectly fired air preheater, a scaled-down utility boiler burner, radiation shields to increase the thermal environment in the combustion chamber, and capabilities to achieve staged combustion.

The system was set up to allow separate delivery of the pulverized coal, RDF and hazardous liquid waste to the combustion chamber. The pulverized coal and the RDF were pneumatically conveyed to the burner using a portion of the combustion air. Exhaust ducts were sized to accommodate isokinetic sampling exhaust particulate emissions. Once the system was checked-out, a systematic set of experiments was conducted which investigated the following variables:

- RDF type
- RDF/coal ratio on a Btu basis
- RDF/coal/hazardous waste ratio
- Excess air

- Staged combustion
- Hazardous waste type

During the experiments the combustion products were monitored for O_2, CO_2, CO, NO, SO_2, SO_3, opacity, particulate loading, particulate size distribution, trace element, and halogen emissions.

RESULTS

RDF Fuel Handling and Combustion Characteristics

Two different types of RDF were utilized in this program; one RDF can be referred to as a powder and the other a fluff.

The powder RDF was easily combusted when co-fired with coal in the suspension firing boiler to heat input fractions of 50 percent RDF. The maximum feed rates to the boiler were limited by the fuel supply systems available for the program rather than any combustion characteristics of the RDF fuel.

With the fluff RDF it was not possible to achieve complete combustion of the RDF in suspension firing above about 10 percent RDF (on a heat input basis). At feed rates approaching 20 percent the RDF burned partly in suspension and partly on the floor of the combustion chamber. The fuel feed system for the fluff RDF was not capable of transporting the plastic materials found in this type of RDF. Heavy duty plastic trash bag liners were particularly difficult to shred and thus caused numerous solid handling and transport problems.

Emission Characteristics

Base Coal--

The base coal was fired at excess air levels between 20 percent and 70 percent for single-stage combustion and at a fixed excess air level of approximately 30 percent with staged combustion. Emission characteristics were determined for gaseous and solid components as a basis of comparison for the co-fired and tri-fired tests.

Co-fired Fuels--

Two different RDF's and two different hazardous waste liquids were co-fired with the base coal. The criteria emissions were measured for all test points. These emissions showed the nitric oxide emissions in all cases to be lower than for the base coal. Carbon monoxide emissions were unchanged and sulfur oxide emissions were lower as compared to the base coal.

Limited trace element measurements and halogen emission measurements were made. The majority of these measurements were made for various percentages of the two RDF's co-fired with coal. It was found that chlorine was the major halogen emission and the concentration increased as the percentage of RDF fired was increased. Principal trace elements found in the flue gas were those present in the RDF and coal. Analyses for polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and dioxins, showed concentrations were well below levels of concern for all conditions sampled.

Tri-fired Fuels--

Tri-firing was accomplished for each of the two hazardous waste liquids (benzene and waste lubricating oil) in combination with coal and the powder RDF.

The conclusions from the measurements made during these experiments are the same as for the co-fired fuels.

CONCLUSIONS

The major conclusions that can be drawn from the results of the study include:

- The fluff type RDF did not exhibit acceptable combustion characteristics at RDF/coal ratios above 10 percent (on a heat input basis) with pulverized bituminous coal.

- The powder RDF exhibited suitable combustion characteristics when co-fired in suspension firing at ratios up to 50 percent (on a heat input basis) with pulverized bituminous coal.

- Staged combustion was effective in reducing nitric oxide emissions for both RDF/coal combinations. The particulate emissions increased with staged combustion.

- The trends observed in NO_x emissions versus excess air were similar for coal only, co-fired and tri-fired combustion. A slightly lower nitric oxide emission for multifuel combustion compared to coal-only combustion was observed.

- Changes in the trace element concentrations due to co-firing or tri-firing were detected. The increase in chlorine emissions were comparable to the increase in chlorine content of the RDF relative to the coal.

- Acceptable levels of PCB's, PAH's, and dioxins were found for all conditions tested.

SECTION 1.0

INTRODUCTION

Solid waste burning is not a new concept. In the past, incinerators to burn municipal waste were common in most metropolitan areas. With the passage of stringent air pollution regulations and the advent of the sanitary landfill, burning refuse lost much of its widespread application. Recently, however, new incentives have surfaced which again make the combustion of municipal waste an attractive disposal alternative. Today's proposed and prototype installations are processing and preparing the solid waste in a variety of schemes that may shred, compact, or pelletize the refuse into a valuable fuel. Resources in the waste stream are recovered and conservation of other energy sources are realized by the use of this alternate fuel.

Many municipalities are faced with serious solid waste disposal problems while at the same time fuel supplies for industrial and utility boilers have either diminished or experienced a rapid price escalation. An attractive solution to both the disposal problem and the energy problem is the proposed co-firing of municipal solid waste with conventional boiler fuels provided:

1. Pollution problems are not created that violate current regulations
2. Potential boiler corrosion and erosion problems do not shorten the expected boiler life
3. Boilers can be adapted with minimum modifications and the user/producer costs and/or cost savings are mutually attractive

Three basic modes of combustion are represented by current or expected boiler designs. They are:

- grate or bed burning
- suspension burning
- fluidized media burning

Briefly, these three modes can be individually characterized by the type of conventional fuel that is burned. Coal-stokers represent the major category of bed burning equipment for industrial steam production. Stokers are manufactured with a variety of fuel systems and grate designs. A popular design is the spreader stoker in which the coal is thrown onto the grate with a paddle wheel. While spreader stokers are the largest single type of stoker used to burn coal, this design need not be the preferred method of firing RDF. Currently, RDF is fired alone and in combination with coal on overfed traveling grate stokers.

Suspension fired boilers are characterized by pulverized coal, oil and natural gas. In this type of boiler, the fuel is finely divided, pulverized or atomized and injected into the firebox where it burns in suspension. Suspension firing of pulverized coal is most popular in the larger industrial boiler and utility boiler categories. There are several existing suspension fired units with RDF co-fired with pulverized coal and oil.

Fluidized media combustion is characterized by the fluid bed combustor now under development by several boiler manufacturers. These combustors operate with a bed material which is fluidized with the combustion air. The fuel is introduced into the combustor and burns in the bed. Heat is removed by steam coils immersed in the bed. One of the largest on line RDF demonstration plants uses wet process RDF in a fluidized bed combustor.

Two different modes of combustion are represented by the bed burning mode and the suspension burning mode. The combustion in these two extreme cases is such that the emissions from one are not characteristic of the emissions from the other. For example, NO_x emissions from bed combustion are typically 25 to 50 percent of that from a suspension type combustor. For this reason, both bed and suspension combustion modes should be evaluated for their emissions when co-firing RDF. The spreader stoker is a mixture of the two combustion extremes since approximately 30 percent of the fuel burns in suspension above the fuel bed on the grate with the balance burning on the grate. The emissions from this combustion process are therefore not characteristic of either bed or suspension firing.

1.1 BACKGROUND

The combustion of municipal solid wastes in industrial or utility boilers has become an attractive economic alternative when one considers that (Refs. 1,2,3):

- Acceptable sanitary landfills are becoming more difficult to site and only five percent of all current disposal sites meet EPA standards
- The transportation costs to remaining acceptable landfills are becoming enormous
- Incinerators that meet new air pollution standards are too expensive for most communities to seriously contemplate
- Approximately 1.22 x 10^{11} kg of municipal refuse were generated in 1973, 1.44 x 10^{11} kg in 1977, and an estimated 1.81 x 10^{11} kg will be generated by 1985
- The energy equivalent of 24 million cubic meters of oil could be saved if the burnable items, mainly the 3.63 10^{9} kg of plastic and 3.18 x 10^{10} kg of paper, were tapped for their energy content. Even more energy could be saved by recovering valuable metals from refuse instead of producing them from ore
- Approximately 2.3 to 2.7 kg of waste per capita are generated each day with a heating value of between 12,000 to 14,000 kJ/kg
- Municipal solid waste represents a daily replenishable energy source equivalent to 5.6 percent of the energy consumed by all U.S. industries or about 2.0 percent of all the energy consumed in the U.S. Solid fuel-fired boilers, in particular, have the potential of generating about 5.75 percent - 11.9 percent of all industry steam requirements in the U.S. (2.5 percent - 5.2 percent of all industry and 1 percent - 2 percent of all U.S. energy requirements)

Although the incentives and potential benefits of direct combustion of refuse in boilers are becoming more apparent, there are a number of serious limitations that must be explored before this approach can be universally applied. Air pollution concerns are a primary factor and a number of prior studies have attempted to quantify emission factors for various operating conditions. Measurements of the criteria pollutants NO_x, SO_x, CO, hydrocarbons, particulate and HCL have been made on several field operating boilers firing solid waste and co-firing RDF with coal. However, the data are not entirely consistent from test to test and the reasons for the differences are not apparent. Non-criteria pollutants such as POM, PCB and trace elements, have not received much attention from RDF-fired systems yet.

Several government agencies (EPA, ERDA, etc.) and industry associations (National Center for Resource Recovery) have conducted assessments or reviews of these potential problems but very little concrete test data are available. In addition to the EPA studies at Union Electric in St. Louis by MRI and the current Columbus, Ohio program with Battelle, the ERDA Urban Waste Technology Branch has conducted extensive assessments of major European and U.S. waste-to-energy plants, including the plant at Nashville, Tennessee. Unfortunately, severe emission and operational problems were encountered at Nashville including water wall and superheat tube corrosion at comparatively low temperature conditions. A careful review of these plants indicates that emissions, corrosion, and erosion problems can be minimized if one carefully applies an existing knowledge of boiler operation limitations, ash characteristics, combustion optimization, and emissions dependence.

1.2 OBJECTIVES AND APPROACH

The primary emphasis in this study was to characterize the environmental impact (aqueous, air, and solid waste) from the combustion of pure RDF and mixtures of RDF and coal in a suspension fired laboratory boiler.

The objective of the laboratory test program was to investigate the effects of variations in the combustion process on performance and pollutant emissions rates. The major combustion parameters including RDF to coal ratio and excess air were systematically varied for both single stage and two stage combustion conditions. Further experiments to evaluate the potential for tri-firing a hazardous waste oil with coal and RDF were made.

In the suspension burning tests, the laboratory multi-fuel boiler was used to evaluate finely divided RDF and mixtures of RDF and pulverized coal. It was especially pertinent to the current project that this laboratory boiler be used for these tests since this unit has been very well characterized in terms of its combustion parameters as well as its emission of all criteria pollutants and most of the emerging non-criteria pollutants with EPA sponsored programs (EPA 68-02-2144). The burner was a scaled down version of a field operating utility boiler. The combustion characteristics and heat absorption profile with residence time in the boiler are very close to existing utility boilers.

The boiler was capable of modified combustion operation including staged firing for NO_x emissions reductions. Data from this modified combustion mode is valuable if in the future NO_x controls are imposed on RDF fired systems.

SECTION 2.0

EXPERIMENTAL APPARATUS AND PROCEDURE

The objectives of the present program were accomplished through a systematic series of experiments conducted in a pulverized coal combustion facility capable of firing at rates to 880 kW. All of the experiments in the program were at a fixed firing rate of 440 kW. The facility coal burner was modified to provide for co-firing of RDF and coal. Tri-firing was accomplished with an oil atomizer inserted into the combustion zone through the burner flame detector sight tube.

2.1 COMBUSTION SYSTEM

The basic system used for the experiments is shown in Figure 2-1. The system consists of a multi-fuel combustor and baghouse. The basis of the combustion facility is a modified 780 kW firetube boiler. The combustion modeling principles used in designing this facility to simulate combustion conditions in full scale utility boilers are discussed in Reference 4. The apparatus, shown in Figure 2-1, can be divided into five groups of components: (1) fuel supply, (2) air supply, (3) burner, (4) boiler furnace, and (5) instrumentation.

The basic fuel used during these experiments was coal. The coal was pre-pulverized to 75 percent through 200 mesh and was feed into the primary combustion air by means of a vibratory screw type feeder. The primary combustion air fluidized the coal and carried it to the coal burner where the mixture was then tangentially injected into the furnace by the burner. A complete description of the feeder system and the combustion facility is contained in Appendix A. A schematic of the coal feed system is given in Figure 2-2.

The combustion air was supplied from an indirect-fired preheater. The air passed through an insulated duct and a venturi meter to a point where a portion of the combustion air was drawn off and passed through another venturi

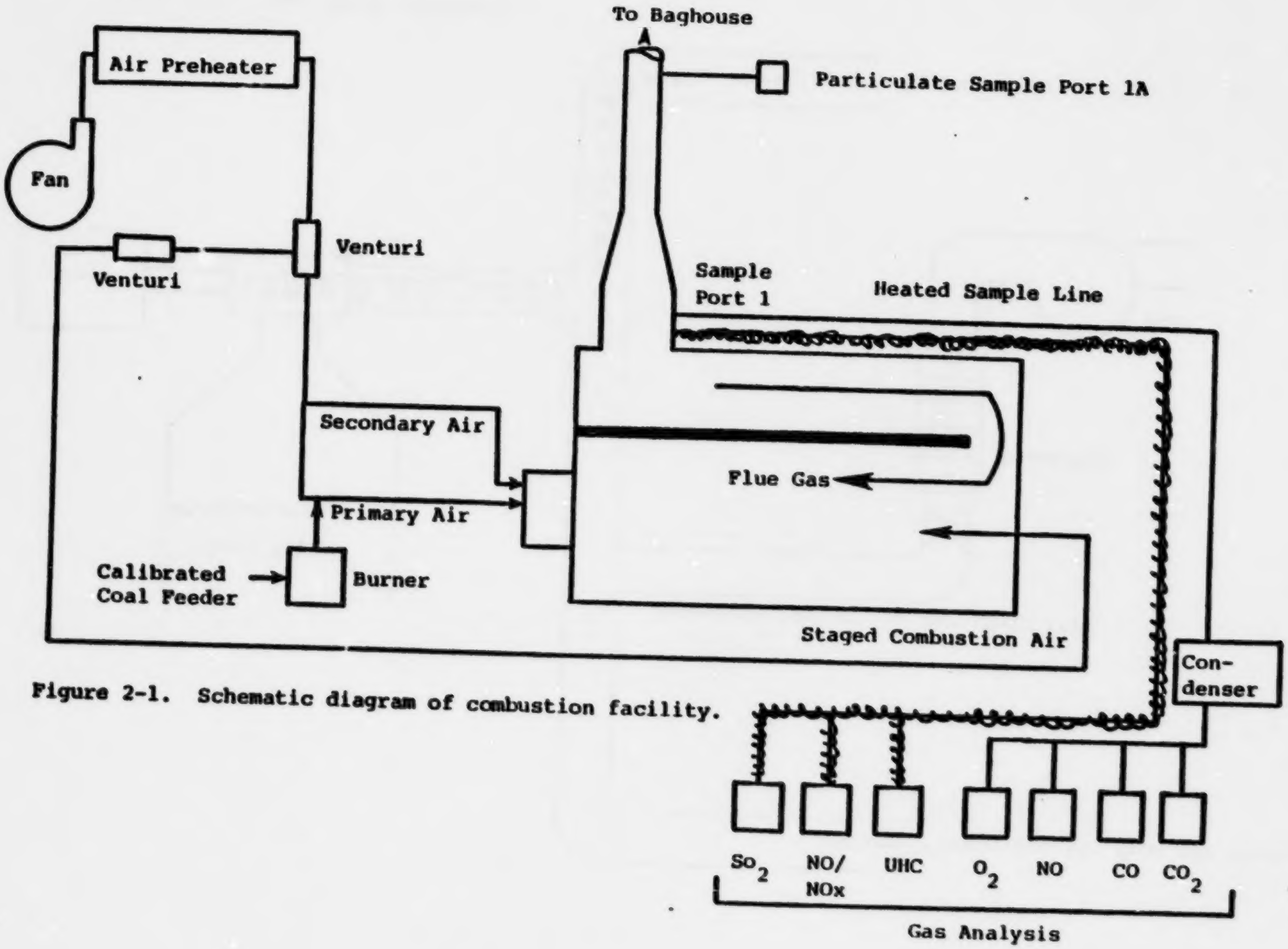

To Baghouse
Particulate Sample Port 1A
Air Preheater
Fan
Venturi
Venturi
Sample Port 1
Heated Sample Line
Secondary Air
Primary Air
Flue Gas
Calibrated Coal Feeder
Burner
Staged Combustion Air
Con-denser
So$_2$
NO/NOx
UHC
O$_2$
NO
CO
CO$_2$
Gas Analysis

Figure 2-1. Schematic diagram of combustion facility.

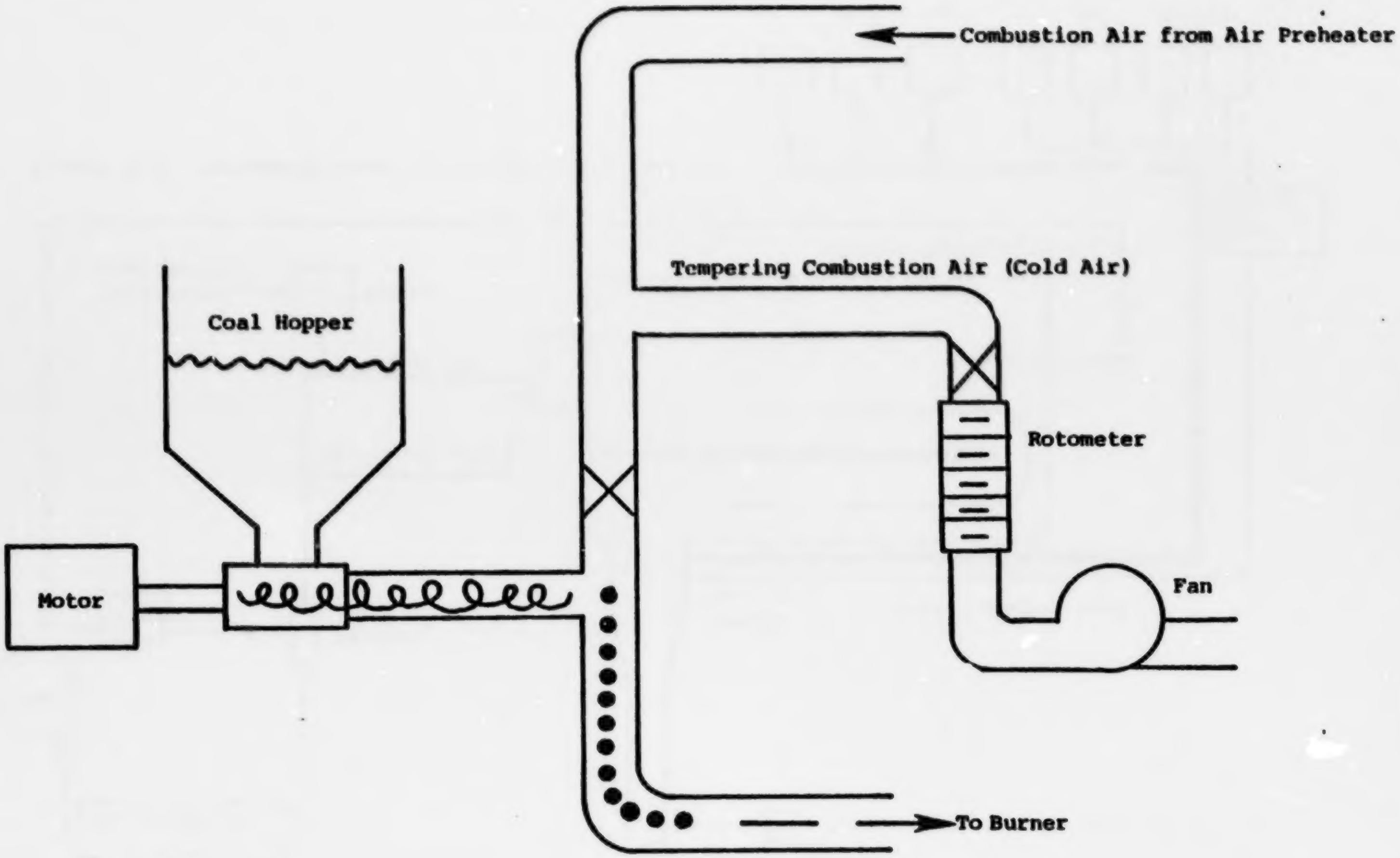

Combustion Air from Air Preheater
Tempering Combustion Air (Cold Air)
Coal Hopper
Rotometer
Fan
Motor
To Burner

Figure 2-2. Coal feed schematic.

meter before joining the tempering air flow from a separate fan. These two streams were joined to form the primary combustion air which then carried the coal to the burner.

The balance of the combustion air from the air heater was used as secondary air for the burner. For tests involving two stage combustion part of this air was diverted through a staged air line and another venturi meter, then to a perforated torus inside the combustion chamber. A schematic of the combustion chamber and combustion air locations is shown in Figure 2-3.

The coal burner was a scaled-down version of a commercial burner presently being used in a utility boiler firing western coal. This burner incorporated adjustable air registers and the primary air/coal stream was mixed with the secondary air by swirling the primary mixture.

The boiler shell was a 780 kW Scotch dry-back type. At a firing rate of 880 kW the boilers volumetric firing intensity was 399 kW/m^3 which is typical of oil-fired utility boilers. The steam produced by this boiler is vented at one atmosphere . The boiler's combustion chamber was fitted with a stainless steel liner to give wall temperatures typical of utility boilers.

2.1.1 RDF Feeders

Two widely different types of RDF's were evaluated in this program. A detailed description of the RDF's can be found in Section 3.0. The Combustion Equipment Associates (CEA) RDF, was a powder and the Continental Can Company's RDF was a fluff. Due to the nature of these materials it was necessary to use two different types of feeders to supply the RDF's to the test boiler. In both feeders fluidizing air was used to carry the RDF into the burner.

2.1.2 Powdered RDF Feeder

The feeder used to carry the powder RDF was a vibratory screw with a live bottom bin, similiar to that used to convey the base coal into the system.

This feeder was configured to be interchanged with the fluff RDF feeder by a minor change in piping. The vibrating screw feeds the RDF into a

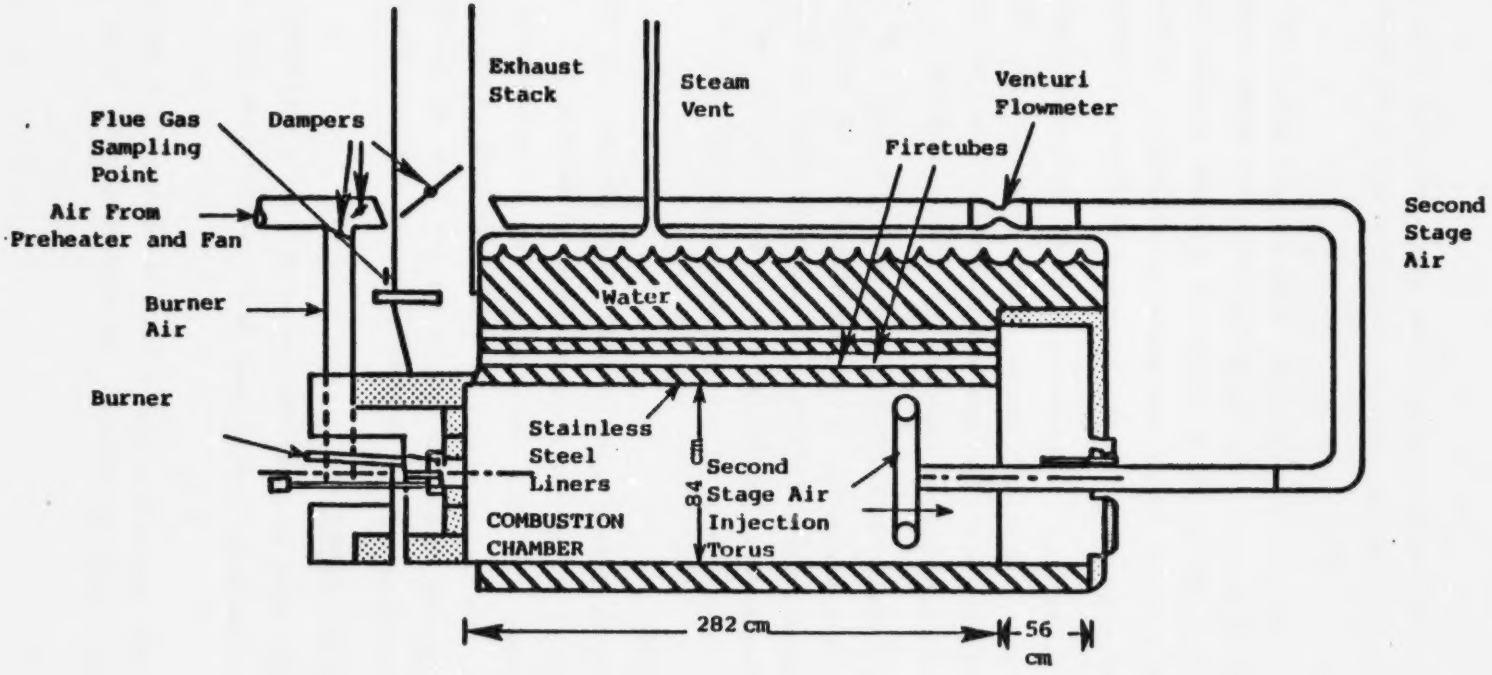

Flue Gas
Sampling
Point
Dampers
Exhaust
Stack
Steam
Vent
Venturi
Flowmeter
Firetubes
Air From
Preheater and Fan
Second
Stage
Air
Burner
Air
Water
Burner
Stainless
Steel
Liners
84 cm
Second
Stage Air
Injection
Torus
COMBUSTION
CHAMBER
282 cm
56
cm

Figure 2-3. Schematic of eighty-horsepower boiler.

drop tube made of plexiglass thus allowing a visual determination of material flow. The falling RDF was then picked up and fluidized by combustion air flowing from yet another supply fan and rotometer. The RDF was then carried into the combustion zone by this air through the RDF burner. A schematic of this system is shown in Figure 2-4.

The combustion air was made to expand at the point where the RDF was entrained. This technique was found necessary to minimize plugging of the fluff type RDF (Ref. 5).

A calibration of the feeder using the powder RDF showed essentially a linear flow relationship with screw speed, however this relationship was not valid when the feeder was coupled to the combustion system. Section 2.0, Experimental Procedure, describe the methods used to determine the RDF mass flows.

2.1.3 Fluff RDF Feeder

The RDF feeder used to feed the fluff RDF was developed by Acurex (Ref. 5). Only minor modifications to this feeder were made for compatibility to the test facility.

This feeder consists of a rotating supply drum which is periodically stopped and charged with RDF, a continuous variable speed conveyor belt, and a pneumatic discharge system for fluidizing the RDF.

One end of the conveyor belt is located axially along the center line of the supply drum. As the drum is rotated it drops the fluff RDF onto the conveyor belt. The conveyor belt then rotates in and out of the drum thus carrying RDF to the discharge port which is located outside of the drum. The RDF is collected by 2.54 centimeters high metal stand-offs which are evenly distributed along the belts surface. A knife edge at the drum exit acts to level the exiting RDF.

As the belt rotates around the drive sprocket at the end of the belt outside the drum, additional combustion air is directed along the belt surface at this point, acting to lift the RDF from the belt and fluidize the RDF.

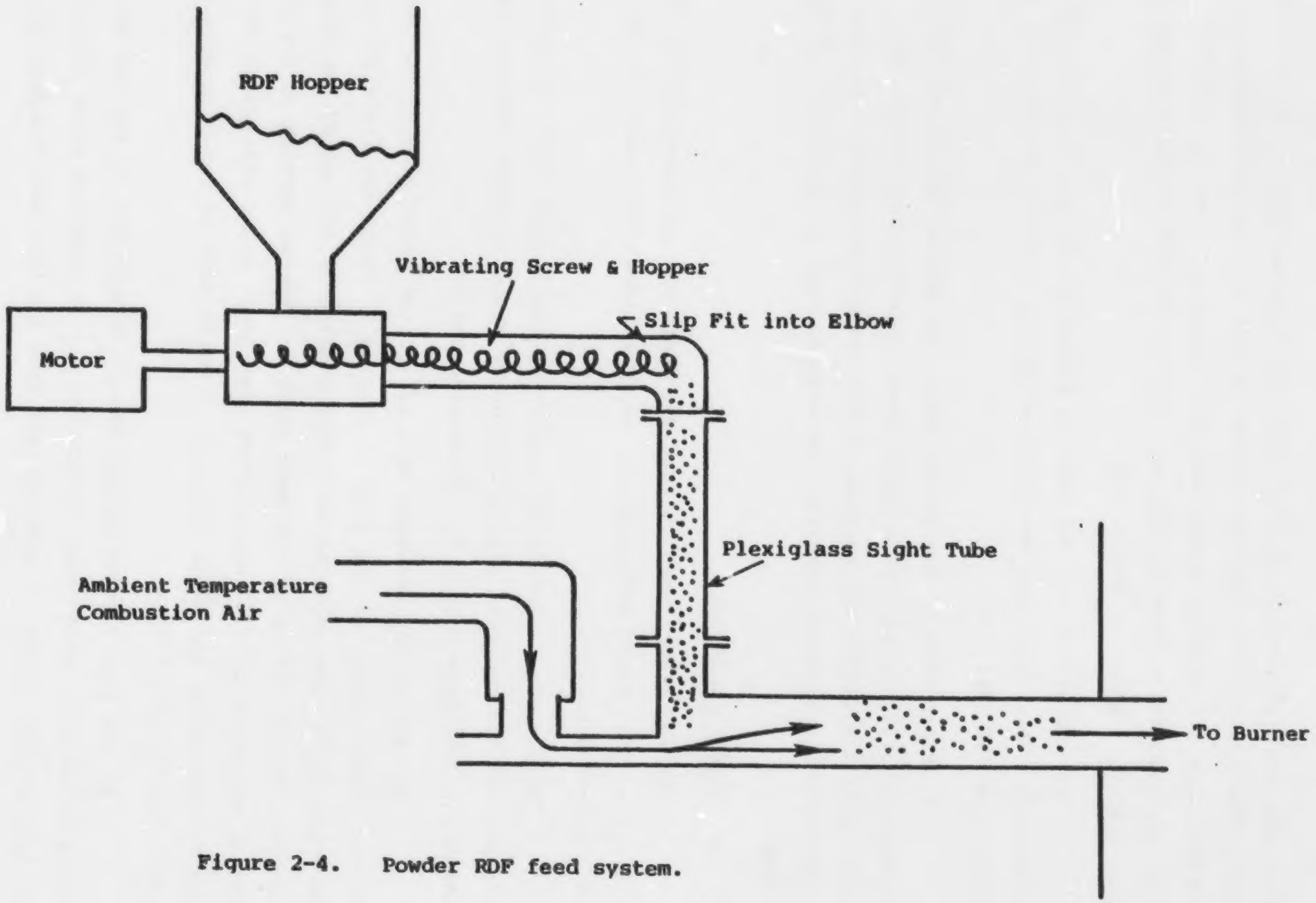

RDF Hopper
Vibrating Screw & Hopper
Slip Fit into Elbow
Motor
Plexiglass Sight Tube
Ambient Temperature
Combustion Air
To Burner

Figure 2-4. Powder RDF feed system.

The fluidized RDF then exits from the feeder system into the sight tube used for the powder RDF. As with powder RDF, additional combustion air is then introduced. This keeps the RDF fluidized and allows the change in flow direction necessary to introduce the RDF into the burner. A schematic of this feed system is shown in Figure 2-5.

Calibration of this feed system using the Americology RDF as received, showed a linear relationship of flow with conveyor belt speed up to 50 percent of maximum RPM. Above this value the relationship became non-linear. Reshredding the RDF using a leaf mulcher reduced the particle size of the RDF and established a linear flow relationship over the entire belt speed range. The flow capacity of the feeder was affected by the moisture content of the RDF. This is discussed under Section 4.0, "Experimental Results."

2.2 BURNER MODIFICATIONS

The original coal burner is shown on Figure 2-6. This burner used a pilot ignitor located on the centerline of the burner as shown. Several arrangements were studied to determine the proper location and means of introducing the RDF through this burner and into the flame zone. Among the methods considered were:

- Mixing RDF and coal
- Tangential entry of the RDF co-axial with coal injection either external or internal concentric flow path with coal flow path
- Axial entry by replacing ignitor with RDF tube

Based upon the experience of Acurex (Ref. 5) where great difficulty was experienced with the fluff type RDF plugging passages it was determined that the axial entry was the most practical method.

Using the axial entry required a minimum number of bends in the flow path and would allow for a straight RDF passage through the burner thus permitting access for prodding to unplug the flow path. Another benefit of this arrangement was thermal shielding of the RDF flow passages by the relatively cool coal/air mixture surrounding the RDF tube.

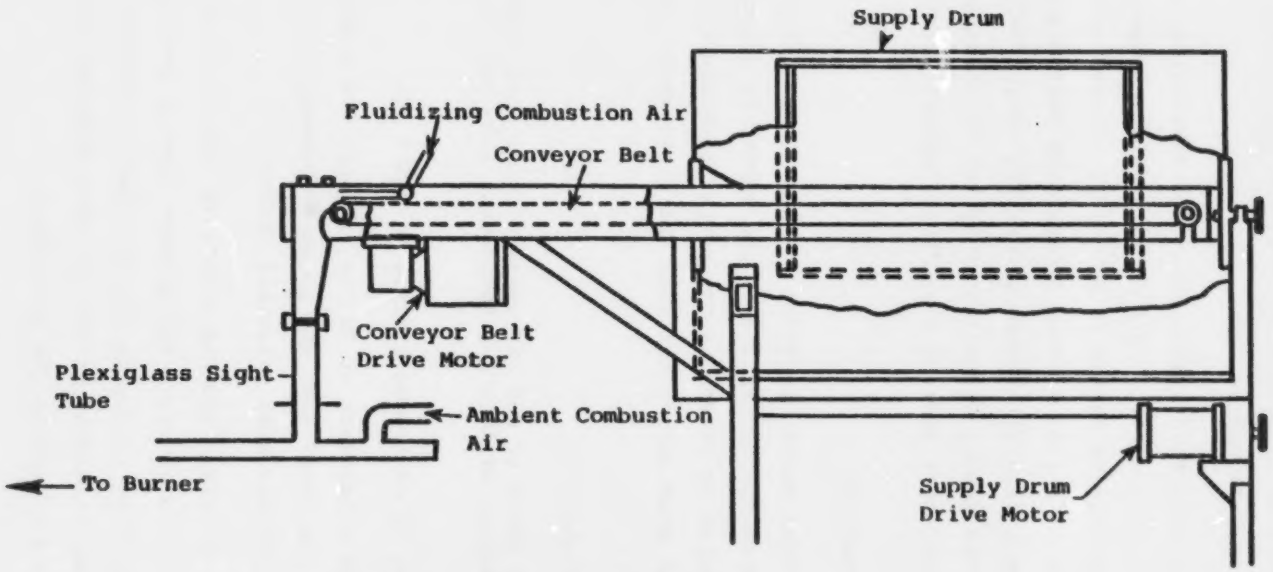
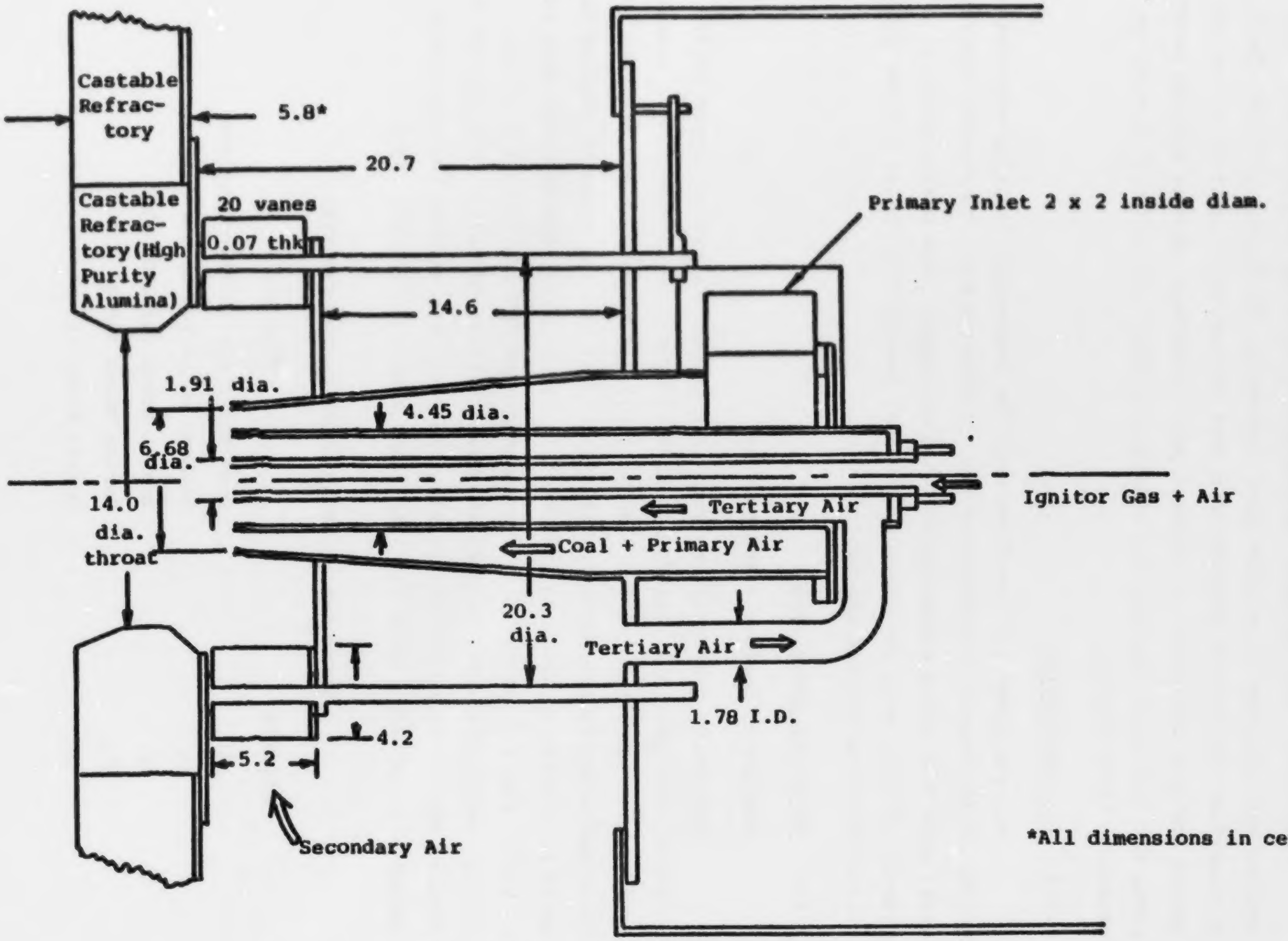

Supply Drum
Fluidizing Combustion Air
Conveyor Belt
Conveyor Belt
Drive Motor
Plexiglass Sight
Tube
Ambient Combustion
Air
To Burner
Supply Drum
Drive Motor

Figure 2-5. Fluff RDF feed system.


Castable Refractory
5.8*
20.7
Castable Refractory (High Purity Alumina)
20 vanes
0.07 thk
Primary Inlet 2 x 2 inside diam.
14.6
1.91 dia.
4.45 dia.
6.68 dia.
14.0 dia. throat
Ignitor Gas + Air
Tertiary Air
Coal + Primary Air
20.3 dia.
Tertiary Air
1.78 I.D.
4.2
5.2
Secondary Air

*All dimensions in centimeters

Figure 2-6. Small-scale version of a full-size coal burner.

The final configuration of the burner is given in Figure 2-7. The ignitor was relocated to a sight port located on the burner mounting flange. By inserting the ignitor through this port satisfactory ignition of the coal burner could be obtained. A similiar port, sometimes used as a flame detector port, was used as a location for inserting a small oil gun when firing the hazardous waste liquid.

2.2.1 Instrumentation

All air flows and gas flows into the combustion facility were measured either by calibrated rotameters or venturi flow meters. Temperature measurements were made using chromel-alumel thermocouples. The measurements of primary interest were the gaseous emissions leaving the boiler and the particulate emissions leaving the boiler.

2.2.2 Emissions Measurement

A. Continuous Gaseous Measurements--

Continuous gas analyzers were used to measure excess oxygen (O_2), oxides of nitrogen (NO), carbon monoxide (CO), carbon dioxide (CO_2), unburned hydrocarbons (UHC), and sulfur dioxide (SO_2). A summary of gas analysis instrumentation is presented in Table 2-1. The gaseous emission samples were taken at the system location indicated in Figure 2-7. Measurements were made at Port 1 for all tests, while Port 1A was used for particulate loading, sizing, sulfur trioxide, halogen and Trace Element Sampling. The SO_2 and UHC samples were obtained by transporting the "wet" gas samples through heated teflon samples lines which fed into a hot pump and selector valve.

TABLE 2-1. GAS ANALYSIS INSTRUMENTATION

Species	Analyzer
NO	Teco Model 10A chemiluminescent
O_2	Beckman Model 742 electrolytic
CO	Horiba Model PIR 2000 NDIR
CO_2	Horiba Model A1A 21 NDIR
SO_2	DuPont Model 401 photometric

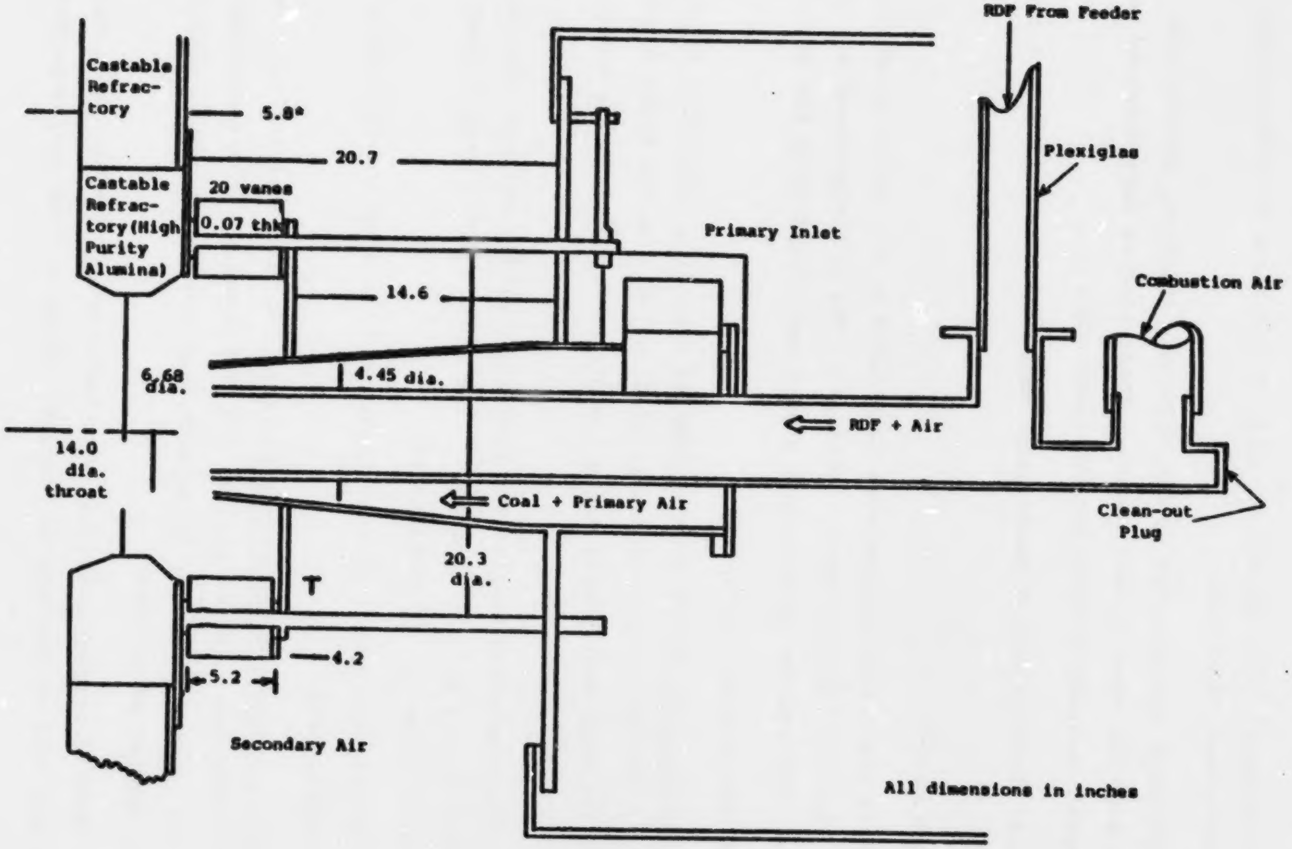

RDF From Feeder
Plexiglas
Combustion Air
Castable Refractory
5.8°
20.7
Castable Refractory (High Purity Alumina)
20 vanes
0.07 thk
Primary Inlet
14.6
6.68 dia.
4.45 dia.
RDF + Air
14.0 dia. throat
Coal + Primary Air
Clean-out Plug
20.3 dia.
4.2
5.2
Secondary Air
All dimensions in inches

Figure 2-7. RDF-coal burner schematic.

B. Batch Gaseous Measurements--

Sulfur trioxide (SO_3) levels for many of the tests were determined using the Goksoyr-Ross Technique.

Concentration measurements of the halogens, chlorine, bromine and florines were made for several test points. These samples were obtained using methods employing analysis by specific ion electrodes.

Detailed descriptions of these batch measurement techniques are given in Appendix B.

C. Particulates--

Particle size distributions were determined at the boiler discharge using an MRI impactor (Cascade type). Details of the procedure used are given in Appendix B. Particulate grain loadings were determined using EPA Method 5.

D. Trace Organics and Inorganics--

1. Sampling methods--Trace element samples including Polycyclic Organic Material (POM), Polychlorinated Biphenols (PCB) as well as the trace metals, were obtained for many test points using a modified High Volume Stack Sampler (HVSS), as shown in Figure 2-8.

This train provided samples for analysis from the cyclone, the filters, the XAD-2 module and the impingers. The XAD-2 modules were changed for use in the train by Battelle Laboratories.

A detailed description of this system and the sampling techniques used are given in Appendix B.

2. Analysis procedures and criteria--Table 2-2 lists the analyses for the modified HVSS samples, selected gaseous and grab samples. These analyses and techniques are Level 1 criteria, along with some additional tests which focus upon certain species of interest.

The Level 1 samples are split into three groups for the inorganic, as well as for the bulk of the organic samples. These are the coarse particulate

TABLE 2-2. TRACE ELEMENT/ORGANICS ANALYSIS

		Source					
Species	Method	Gaseous	Coal	RDF	Coarse Part.	Fine Part.	Gaseous
Inorganic							
HCl (MI)	SI	12					
HF (MI)	SI	12					
HBr (MI)	SI	12					
Li-U Elements	SSMS		1	1	12	12	12
As	AAS		1	1	12	12	12
Hg	AAS		1	1	12	12	12
Sb	AAS		1	1	12	12	12
Organic							
Mass C_8-C_{12}, T CO	GC/FID				12	12	12
Mass gravimetric	Weigh				12	12	
Organic Classes	FTIR				12	12	12
LC Fractions*	Silica gel				12	12	12
Fraction Mass, T CO*	GC/FID				12	12	12
Fraction Mass, Grav*	Weigh				12	12	12
Classes in Fractions*	FTIR				12	12	12
Compounds in Fract's*	LRMS				12	12	12
Organic Chlorine	AAS				12	12	12
POM Species	GC/MS				--	4	--
PCB Class Id.†	GC/EC				--	12	--
Dioxin Species†	GC/MS				--	3	--
PCB Species§	GC/MS				--	3	--

* Level 1 criteria.

† Conducted if organic chlorine >58 µg/m^3 or 0.003 µg/g in solids.

§ Conducted if PCB class concentration >500 µg/m^3 or 0.002 µg/g in solids.

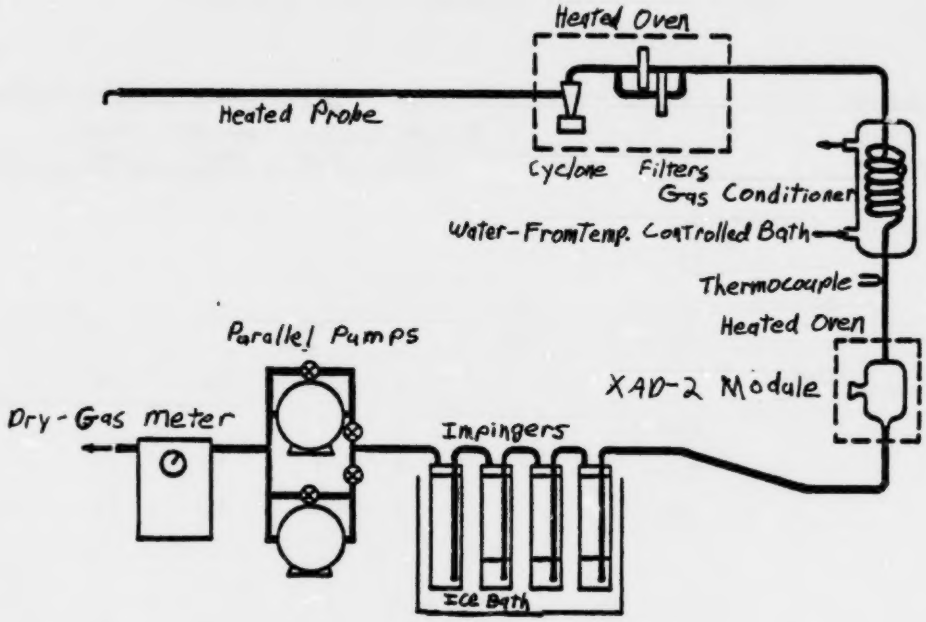

Heated Oven
Heated Probe
Cyclone
Filters
Gas Conditioner
Water-FromTemp. Controlled Bath
Thermocouple
Heated Oven
XAD-2 Module
Parallel Pumps
Dry-Gas meter
Impingers
Ice Bath

Figure 2-8. Modified high volume sampling system.

(>3-5μ), fine particulate (<3-5μ) and gaseous. The gaseous section includes the XAD-2 extractions and appropriate impinger solutions. The train washings were combined into each apprpriate section for analysis.

The bulk of the trace elements were analyzed with spark source spectrometry (SMSS). In addition, the As, Hg, and Sb elements were measured using atomic absorption, as they are not adequately detected with SSMS.

The organic analysis is based on the Level 1 procedure. This method includes many checks to determine if further analysis is worthwhile, avoiding unnecessary costs. This is particularly important since the most comprehensive tests are the most costly, but require an adequate sample for a valid analysis. In addition, tests were included to determine organic chlorine and PCB's. These chlorine compounds are important because of the chlorine content of the RDF. As shown, all tests up to and including the organic chlorine analysis were performed on each sample run.

The last four analyses listed are the extensive POM and PCB tests. Since these are the most costly tests, the samples used here were a composite of the coarse/fine particulates and the gaseous sections of the train. In this manner, the result of these analyses were a total, rather than an unknown fraction of the collected sample (if only one of the three samples was chosen). The POM species analysis was planned for one coal and one of each of these coal/RDF tests. The PCB and dioxin tests are based on a criteria system to avoid unnecessary tests. These cutoff points are those suggested by Battelle and are based on MATES values.

2.2.3 Experimental Procedure

The experimental program required various test procedures depending on the nature of the test point. Typically a full day was devoted to obtaining continuous gas analysis for a test number such as 1 or 5 of the test matrix. In order to obtain data for test numbers such as 2 or 4 it was normally necessary to use two test days, due to the length of sample time required for the various batch samples.

To demonstrate the basic procedure, a description of the methods used to obtain part of test number 32 follows.

On the day preceding the test day all elements of the HVSS were cleaned and prepared. Filters, requiring tare weights, were tared and desiccated.

On the day of the test the boiler was fired using the base coal at the nominal firing rate of 440 kW. The start up and warm-up procedure lasted about 1-1/2 hours. During the boiler warm-up period the sample trains were set-up, leak-checked and heated to operating temperatures.

Upon achieving boiler steam, final adjustments were made to all air flows to insure on point condition. The continuous gas analyzers were calibrated and the facility was ready for adjustment to obtain the tri-firing test point.

This test required 10 percent benzene, 10 percent CEA RDF and 80 percent coal all as a percentage of heat input of 440 kW. The benzene was supplied from a 19 liter can by means of a calibrated constant displacement piston type pump. Thus the flow rate of benzene was fixed and known.

The benzene atomizer was inserted into the boiler, the coal feeder flow was reduced proportionately to account for the benzene using the coal feeder calibration curve. The excess oxygen (O_2) was tracked on a recorder as coal feed rate was reduced, as soon as the change in O_2 reflected the full change in coal feed rate the benzene pump was started. Again excess O_2 was tracked until the system stabilized. At that time the coal feed was again reduced to allow for the RDF, again O_2 was tracked and the RDF feed was started and brought up to a setting which brought the excess O_2 back to the original coal only setting (~5.5 percent).

With the combustion system on line the sampling was started using the HVSS. The sample time required was normally 2-1/2 hours provided all boiler fuel feed settings remained on line. If a fuel feed system malfunctioned then sampling was stopped until the malfunction was corrected. Typically feed malfunctions were confined to the RDF feed systems.

Simultaneous with the sampling using the HVSS, sampling for the halogens was accomplished. Continuous gaseous emission data was taken at the start and end of the HVSS sample.

At the end of the test run the HVSS sample gear was disassembled and cleaned per the established procedures. The test boiler was shut down.

SECTION 3.0

TEST MATRIX

3.1 TEST NUMBERS

The test program consisted of evaluations of the following variables:

- RDF type
- RDF/coal ratio on a Btu basis
- RDF/coal/hazardous waste ratio
- Excess air
- Staged combustion
- Hazardous waste type

Evaluations of each variable consisted of emission measurements as shown in the test matrix Table 3-1. Test numbers 38, 39 and 40 were added late in this program because of the increased interest in hazardous waste disposal.

3.2 TEST FUELS

The coal and RDF fuels used in the program were supplied to all three contractors participating in this EPA project. The coal and RDF fuel for each contractor came from the same respective sample. This was done to minimize the test fuels as a variable between the three different modes of combusting the coal and RDF.

The hazardous waste used was selected by each contractor on approval of the EPA Project Officer. The selection of the type of hazardous waste was based partially on the compatibility with the modes of combustion employed and on the availability of the hazardous waste.

TABLE 3-1. TEST MATRIX

Test No.	Fuel Type	Combustion Conditions Excess O_2	Single Stage	Two Stage	Cont. Gas Analysis	Particulate Loading	Emission Measurements Particulate Size	POM PCB	Metals	CD BB P	Baghouse Ash Sample	Bottom Ash Sample	SO_3
1	Coal	2,4,6,8	X		X								
2	Coal	6	X		X	X	X	X	X	X	X	X	X
3	Coal	2,4,6,8		X	X								
4	Coal	6		X	X	X	X	X	X	X	X	X	X
5	10%*RDF80 (1)	2,4,6,8	X		X								
6	10%	6	X		X	X							
7	20%	2,4,6,8	X		X								
8	20%	6	X		X	X							
9	50%	2,4,6,8	X		X								
10	50%	6	X		X	X							
11	Max %	2,4,6,9	X		X								
12	Max %	6	X		X	X	X	X	X	X	X	X	X
13	Opt %	6	X		X	X	X	X	X	X	X	X	X
14	Opt %	2,4,6,8		X	X								
15	Opt %	6		X	X	X	X	X	X	X	X	X	X
16	5%RDF82 (2)	2,4,6,8	X		X								
17	*5%	6	X		X	X							
18	10%	2,4,6,8	X		X								
19	10%	6	X		X	X							
20	15%	2,4,6,8	X		X								
21	15%	5	X		X	X							
22	Max %	2,4,6,8	X		X								
23	Max %	6	X		X	X	X	X	X	X	X	X	X
24	Opt %	6	X		X	X	X	X	X	X	X	X	X
25	Opt %	2,4,6,8		X	X								
26	Opt %	6		X	X	X	X	X	X	X	X	X	X
27	Coal + 5%HW	2,4,6,8	X		X								
28	Coal + 10%HW	2,4,6,8	X		X								
29	Coal + 10%HW	2,4,6,8	X	X	X								
30	Coal + 10%HW	6	X		X	X	X	X	X	X	X	X	X
31	C+10%CEA+10%HW	2,4,6,8	X		X								
32	C+10%CEA+10%HW	6	X		X	X	X	X	X	X	X	X	X
33	C+OptCEA+10%HW	2,4,6,8	X		X								
34	C+OptCEA+10%HW	6	X		X	X	X	X	X	X	X	X	X
35	Coal	2,4,6,3	X		X								
36	Coal	6		X	X	X	X	X	X	X	X	X	X
37	C+20%CEA	3,4,5,6,8	X		X					X			
38	C+40%CEA+10%WO	6	X		X	X	X	X	X	X	X	X	X
39	C+20%WO	6	X		X	X	X	X	X	X	X	X	X
40	C+40%CEA+20%WO	6	X		X	X	X	X	X	X	X	X	X

*Balance coal on Btu basis

(1) CEA RDF

(2) Americology RDF

The test coal was a Kentucky bituminous coal. The coal was prepulverized to the nominal fineness used by suspension fired coal systems, typically 70-80% through a 200 mesh.

RDF #1 was the Combustion Equipment Associates fuel known by the trade name of ECO II. This fuel is derived from municipal wastes. After separation of non-combustibles, an embrittlement process is then followed by a pulverization process thus yielding the final product. ECO II has the appearance of a coarse powder and has a low initial moisture content. The sample used for these tests came from a pilot plant run that was made to duplicate ECO II being produced by a commercial plant.

RDF #2 was American Can Company's fuel designated as Americology. This fuel is also derived from municipal waste. This fuel is described as a fluff as compared to the ECO II powder. This RDF had a lower moisture content than was expected (9% vs. 20%), however the particle size was such that initial feeder calibrations defined the need for further shredding, therefore a final shredding of the material reduced the paper and hard plastics to about a 1.3 x 1.3 cm size.

Before these RDF fuels could be brought into the state of California it was necessary to demonstrate compliance with the state of California Department of Food and Agriculture regulations. The CEA RDF was certified by the state of California based upon the information supplied by CEA which described their manufacture process and in-house testing. The Americology RDF was fumigated outside the state of California using the procedure recommended in the U.S. Department of Agriculture Plant Protection and Quarantine Manual, T403(e)-(2) Section 6, Page 6. This treatment is methylbromide fumigation under a tarpaulin using 4.5 kg of methylbromide per $28 m^3$ of RDF at NAP for 48 hours at 278°K or above.

After inspection and approval by the Agricultural Department the RDF was stored indoors in the original shipping containers until used.

The hazardous wastes tested were benzene and waste lubricating oil. The benzene was commercial grade benzene used in the paint industry. The waste lubricating oil came from a local concrete sales plant which maintains a fleet of concrete trucks, primarily diesels.

A sample of the base coal and the CEA-RDF was analyzed for mercury, arsenic and antimony using atomic absorption spectrophotometry (AAS). The results of those analyses are given in Table 3-2.

TABLE 3-2. AAS ANALYSIS FOR MERCURY, ARSENIC AND ANTIMONY OF FUEL SAMPLES

Sample I.D.	Mercury (μg/g)	Arsenic (μg/g)	Antimony (μg/g)
Coal	0.05	4.6	<2.0
Refuse Derived Fuel	0.31	1.0	<2.0

All fuels except the benzene were analyzed by certified commercial testing laboratories for both physical and chemical properties.

A comparative tabulation of selected properties is given in Table 3-3. The ranges of composition shown for the coal and CEA RDF illustrate the variation in samples analyzed for various dates.

TABLE 3-3. FUEL ANALYSIS (AS RECEIVED)

	Coal	CEA RDF	Americology RDF	Waste Oil
Proximate Analysis (wt,%)				
Moisture	3.51-4.20	--	8.72	--
Ash	7.63-8.97	--	14.86	--
Volatile	36.11-36.50	--	66.68	--
Fixed Carbon	50.87-52.36	--	9.74	--
Sulfur	0.77-1.07	--	0.26	--
HHV (kJ/kg)	29510-30256	--	16944	--
Ultimate Analysis (wt,%)				
Moisture	3.51-4.20	2.99-3.53	8.72	--
Carbon	71.31-73.54	41.64-44.16	37.94	83.63
Hydrogen	4.71-4.88	5.3-5.51	4.91	12.89
Nitrogen	0.98-1.29	0.24-0.34	0.67	0.064
Chlorine	0.04-0.06	0.16-0.26	0.53	(66ppm)
Sulfur	0.77-1.07	0.77-1.16	0.26	0.47
Ash	7.63-8.97	11.45-14.13	14.86	0.79
Oxygen (diff)	8.16-8.74	32.76-34.63	32.11	2.16
Ash Mineral Content (wt,%)				
SiO_2	51.47-53.14	53.61-55.82	55.82	--
Al_2O_3	26.48-31.27	9.43-10.93	10.92	--
T_1O_2	1.31-1.60	1.22-1.36	1.58	--
Fe_2O_3	8.72-13.69	7.86-9.32	3.41	--
CaO	0.78-1.48	9.34-9.6	11.13	--
MgO	0.53-0.82	1.55-1.94	2.26	--
K_2O	1.47-1.68	1.54-1.71	1.63	--
Na_2O	0.03-0.93	5.82-6.81	7.51	--
SO_3	1.05-1.14	3.47-7.32	1.59	--
P_2O_5	0.09-0.11	0.71-0.80	0.96	--
SrO	0	0.02-0.04	0.00	--
BaO	0.08-0.09	0.14-0.17	0.11	--
Mn_3O_4	0.08-0.17	0.23-0.25	0.20	--
Undetermined	0-0.51	0	2.88	--

SECTION 4.0

EXPERIMENTAL RESULTS

4.1 BURNER CONFIGURATION AND PERFORMANCE

A series of experiments were conducted to determine the most satisfactory air flow distributions between the secondary, the primary, and the RDF combustion air streams. Once the near optimum distributions were found, all experiments were conducted using the same distributions. Thus, for the coal only test points, combustion air was flowing not only through the secondary and primary streams, but also through the RDF stream. In staged combustion, the portion of air used as staging air was diverted from the secondary air, thus maintaining the fluidizing capability of both the RDF and primary streams.

4.2 COMBUSTION CHARACTERISTICS AND GASEOUS EMISSIONS

Various combinations of the test fuels were evaluated. This ranged from base coal only combustion to tri-firing of the base coal with one RDF type (fluff) and Hazardous waste oil. The results of all gaseous test results are presented in this subsection. The presentation for each combination of fuels will discuss, in order, the effect of excess air, the effect of staged combustion and the effect of percent RDF or Hazardous waste, whichever is applicable.

4.2.1 Base Coal

A. Effect of Excess Air--

Baseline tests were conducted to establish gaseous emissions as well as particulates for 100 percent coal firing. It was found that there was an increase in nitric oxide emissions with increasing excess oxygen that varied between 50 to 70 ppm for each one percent increase of excess oxygen. At high excess oxygen levels there were large variations in the nitric oxide emissions. It is believed that this variation was due in part to variations in the nitrogen content of the coal as shown in Table 3-2. The nitric oxide variations are shown in Figure 4-1 for all single stage combustion points.

The sulfur dioxide emissions for these data points are more consistent than the nitric oxide emissions with excess air variations as seen in Figure 4-2. Calculations of sulfur dioxide emissions based upon the fuel analysis are in the range of the measured values at the various excess oxygen levels.

The minimum operating excess oxygen point varied between 3.2 and 4.5 percent. Operation at levels lower than this produced excessive carbon monoxide and opacity. For all conditions where extensive sampling was required, the range of excess O_2 which was set was intended to be 6 percent based upon these baseline points.

B. Effect of Staged Combustion--

A series of staged combustion tests were conducted in which the overall excess oxygen in the stack was held constant while the air flow split between the burner and the staging ring was varied. Gaseous data were obtained for four values of excess oxygen within the range of 4.5 and 8.8 percent O_2. These data show reductions in nitric oxide emissions between 50 and 64 percent as the percent of theoretical combustion air at the burner was reduced. These data are shown in Figure 4-3. The carbon monoxide (CO) concentrations were below 180 ppm for all conditions.

Particulate sizing and loading as well as trace element, halogens and polycyclic samples were obtained for both staged and non-staged conditions. Those results will be discussed and compared to similar samples taken for all co-firing tests in another part of this section.

4.2.2 CEA-RDF/COAL

Three RDF/coal combinations were evaluated; the intended percentages of RDF were 10, 20, and maximum. It was found that the maximum percentage of CEA that could be fired (50 percent) was limited by the RDF feed system supply

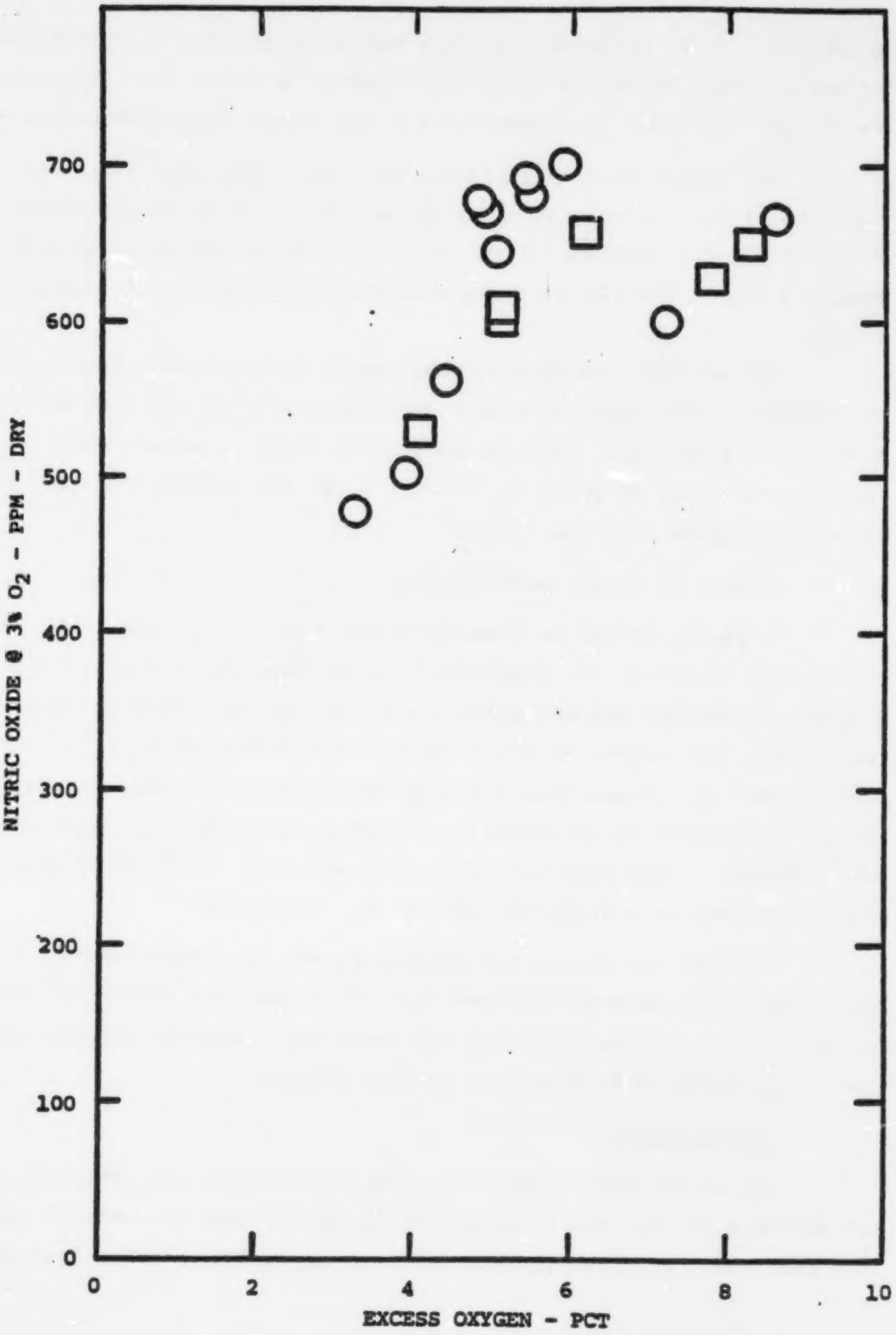


Figure 4-1. Nitric oxide emissions coal - single stage combustion.

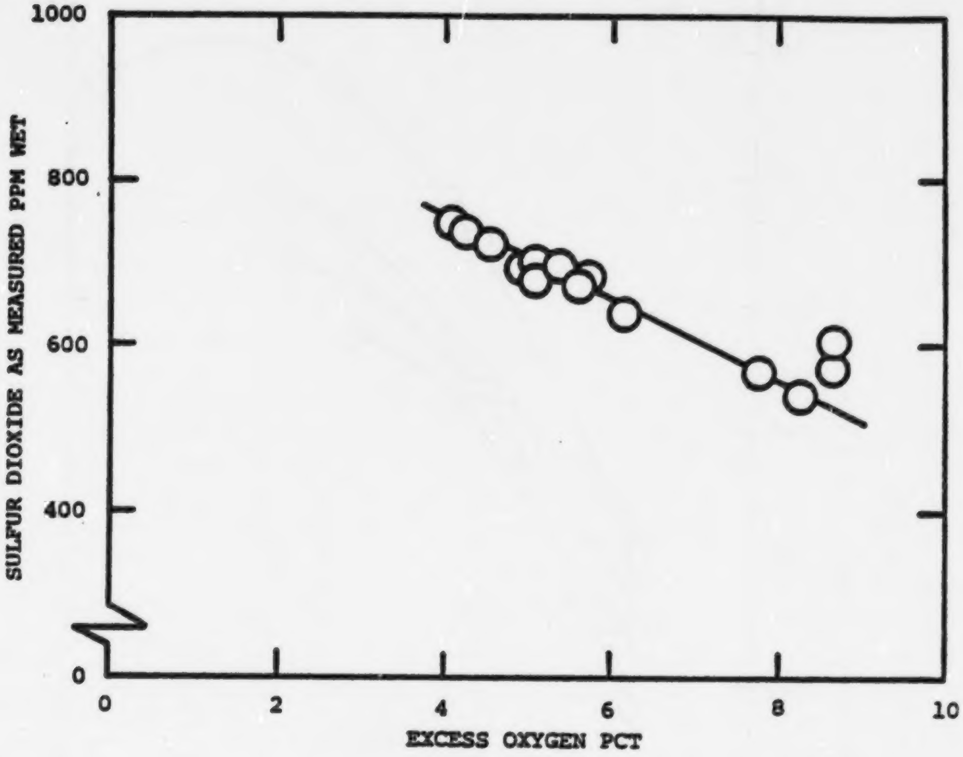


Figure 4-2. Sulfur oxide emissions - coal.

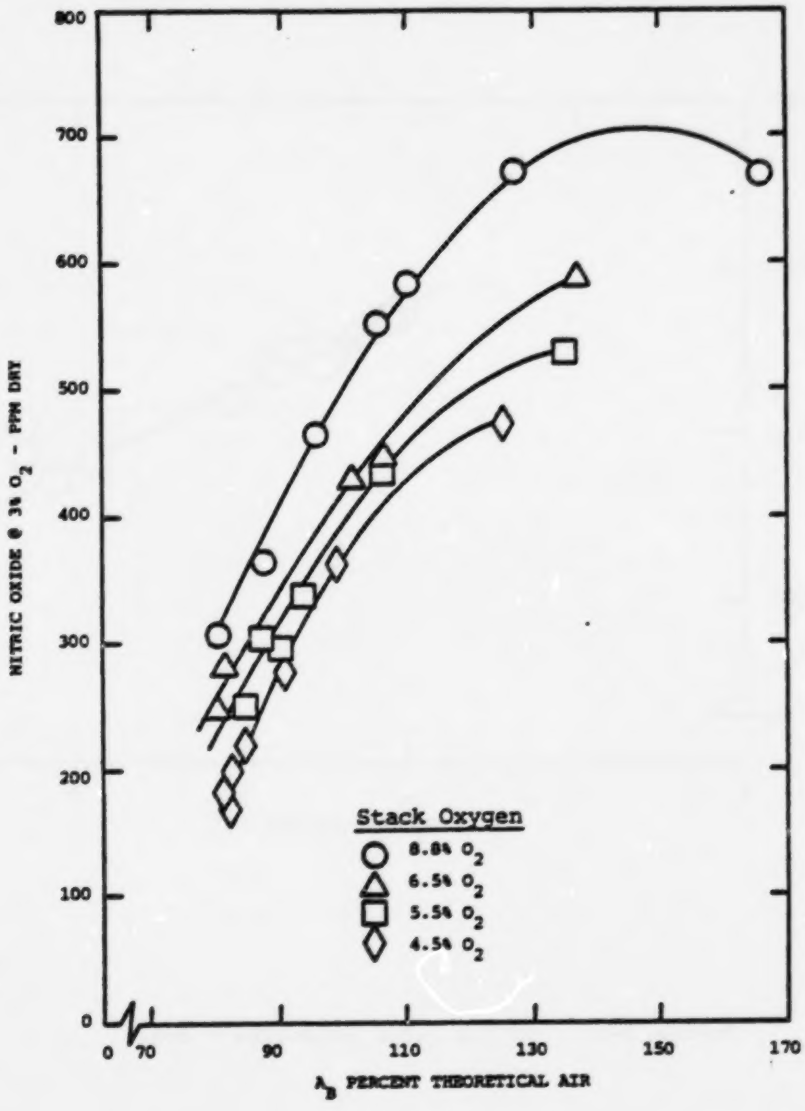


Figure 4-3. Nitric oxide emission - coal - staged combustion.

capability, not by combustion characteristics. Gaseous data were obtained for single stage combustion at three percentages of RDF and staged combustion data were obtained for the maximum percentages.

A. Effect of Excess Air--

When co-firing the CEA-RDF and coal, it was found that the effect of excess air was similar to that of coal only firing. The minimum operational O_2 was essentially the same and the sensitivity of the nitric oxide emissions to excess oxygen was similar. The NO emissions are shown in Figure 4-4. It can be seen that the nitric oxide emissions are slightly lower for co-fired conditions than for coal only firing. This effect can be attributed primarily to the reduced nitrogen content of the RDF--~0.3 percent vs. ~1.1 percent for the coal. Further reductions would be anticipated at percentages greater than 50 percent and particularly as the co-firing shifted toward 100 percent CEA-RDF, as indicated by the emissions of the CEA-only, firing at the reduced firing rate when concentrations of ~250 ppm NO were measured at 6 percent O_2. The higher oxygen availability in the coal air stream as the percentage of coal was reduced, produced more NO, thus offsetting the effect of the reduced nitrogen content effect of the RDF.

Chlorine, fluorine, and bromine measurements were made as indicated in the test matrix. However, the resulting concentrations especially those of the chlorine, indicated some inconsistencies. A special set of test points were evaluated to determine the influence of excess air on the chlorine emissions. The results of those experiments are shown in Figure 4-5. It can be seen that the chlorine emission increase with increasing oxygen availability. No explanation is offered to account for this observation. The variation in chlorine content of the RDF is also a factor which affects the emissions; the fuel analysis shows a 63 percent variation in chlorine for the samples analyzed.

B. Effect of Percent RDF--

The effect of percent RDF upon the nitric oxide emission was discussed above. This effect can be summarized as follows:

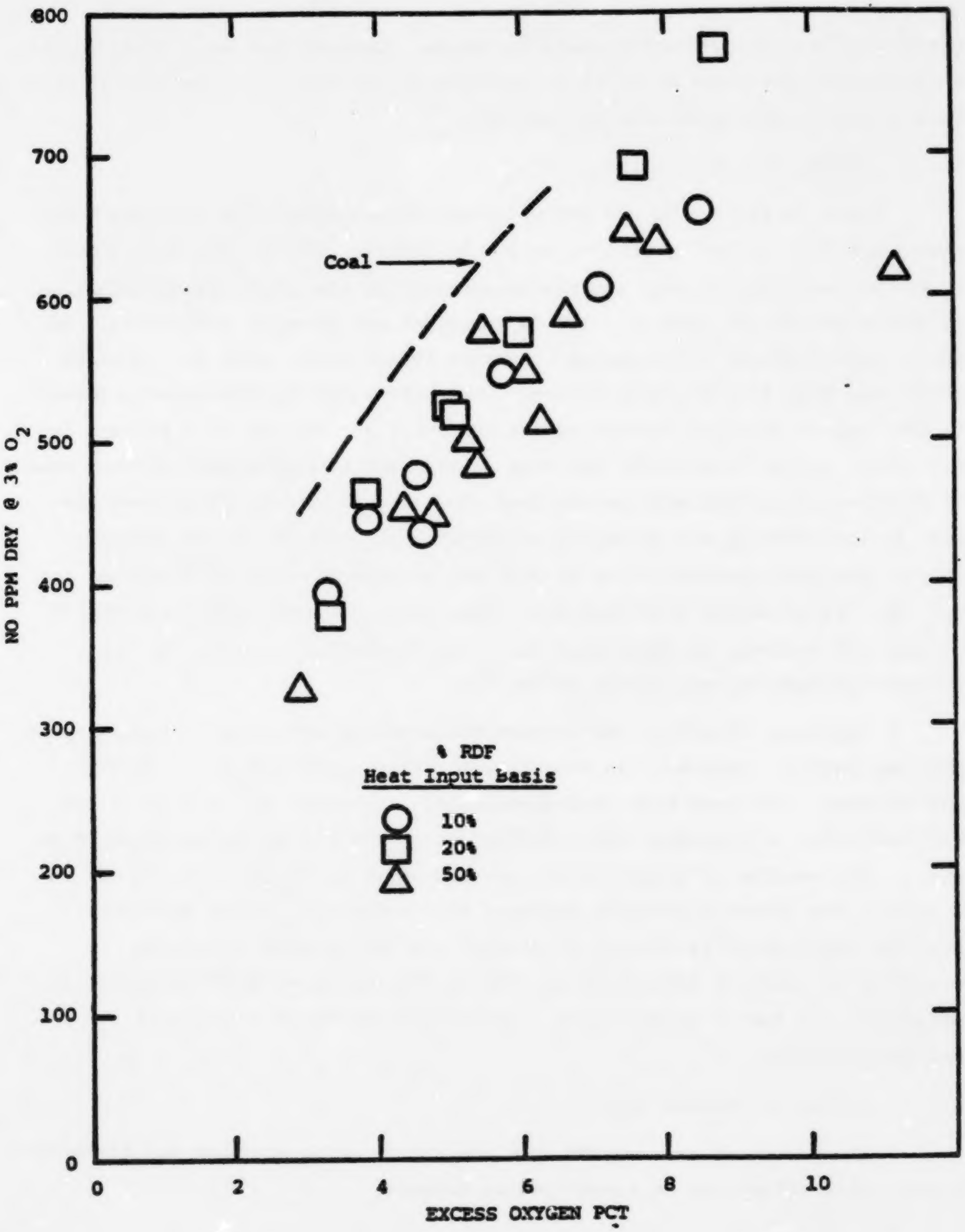


Figure 4-4. Effect of CEA RDF fraction on nitric oxide emissions. Single stage combustion.

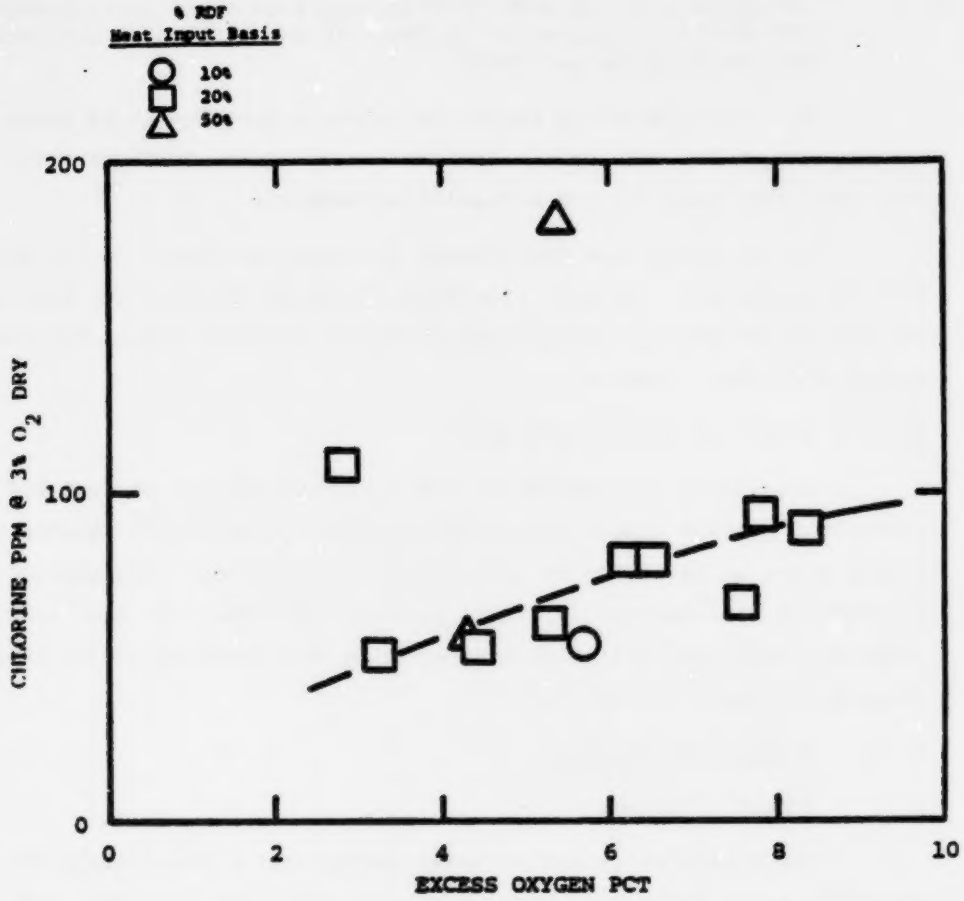


Figure 4-5. Effect of CEA RDF fraction on chlorine emissions.

> There is a slight reduction in nitric oxide emission due to co-firing coal and RDF; however, there is essentially little difference in this effect between 10 and 50 percent RDF, which was the range investigated.

The carbon monoxide emissions showed a tendency to be lower when co-firing then for coal only. Because the carbon monoxide emissions for coal only were low, this was not a significant effect.

It was found that the halogen emissions increased as the percentage of RDF was increased. The most significant halogen emission was for chlorine. The effect for various percentages of RDF is shown in Figure 4-6 far approximately 6 percent excess O_2.

C. Effect of Staged Combustion--

Staging of the combustion air when co-firing 50 percent RDF and coal at various overall excess oxygen levels showed significant reductions in nitric oxide emission, up to approximately 70 percent. The absolute NO concentrations were between 25 and 43 percent lower than for coal only staged combustion and were basically unaffected by the level of excess oxygen. These results are shown in Figure 4-7.

4.2.3 Americology RDF/Coal

A. Effect of Excess Air--

The effect of excess air when co-firing the Americology RDF and coal was found to be similar to that previously found for coal only and for CEA-RDF/coal. The minimum operational O_2 was essentially the same and the sensitivity of the nitric oxide emission to excess oxygen was similar as for the CEA-RDF and coal. However, the absolute emissions were not as low as for the CEA-RDF. This is due to the higher nitrogen content of the Americology RDF (0.67 percent vs. 0.29 percent) than that of the CEA-RDF. The nitric oxide emissions are shown in Figure 4-8.

The influence of the excess air on chlorine emissions was not investigated for this RDF as it was for the CEA-RDF.

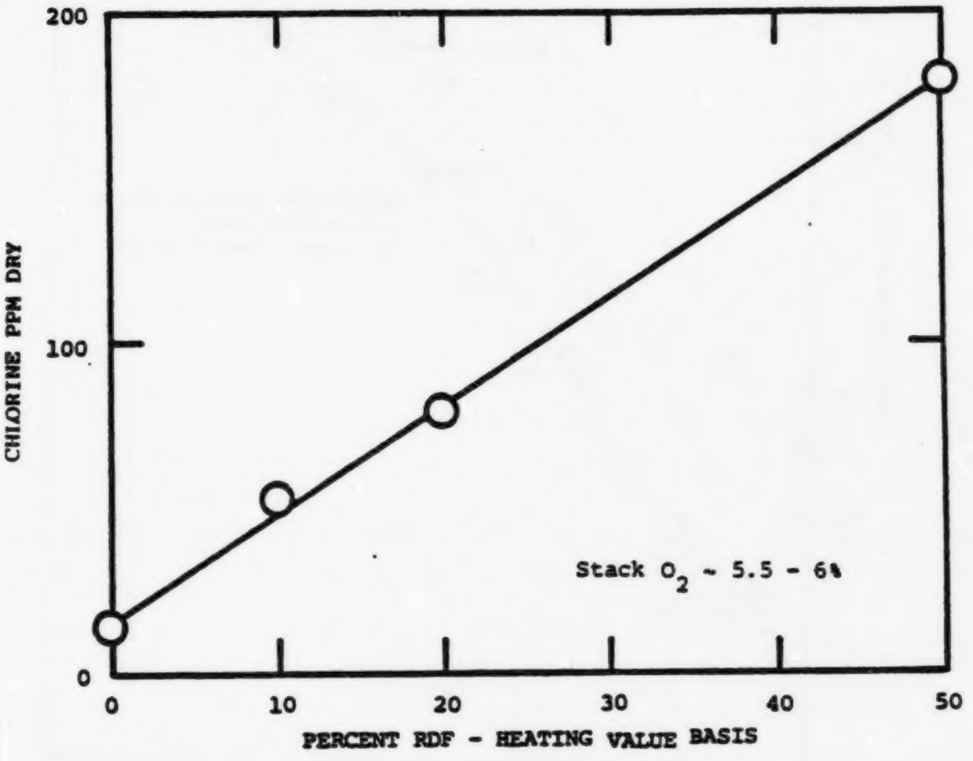


Figure 4-6. Chlorine emissions co-fired CEA RDF and coal. Single stage combustion.

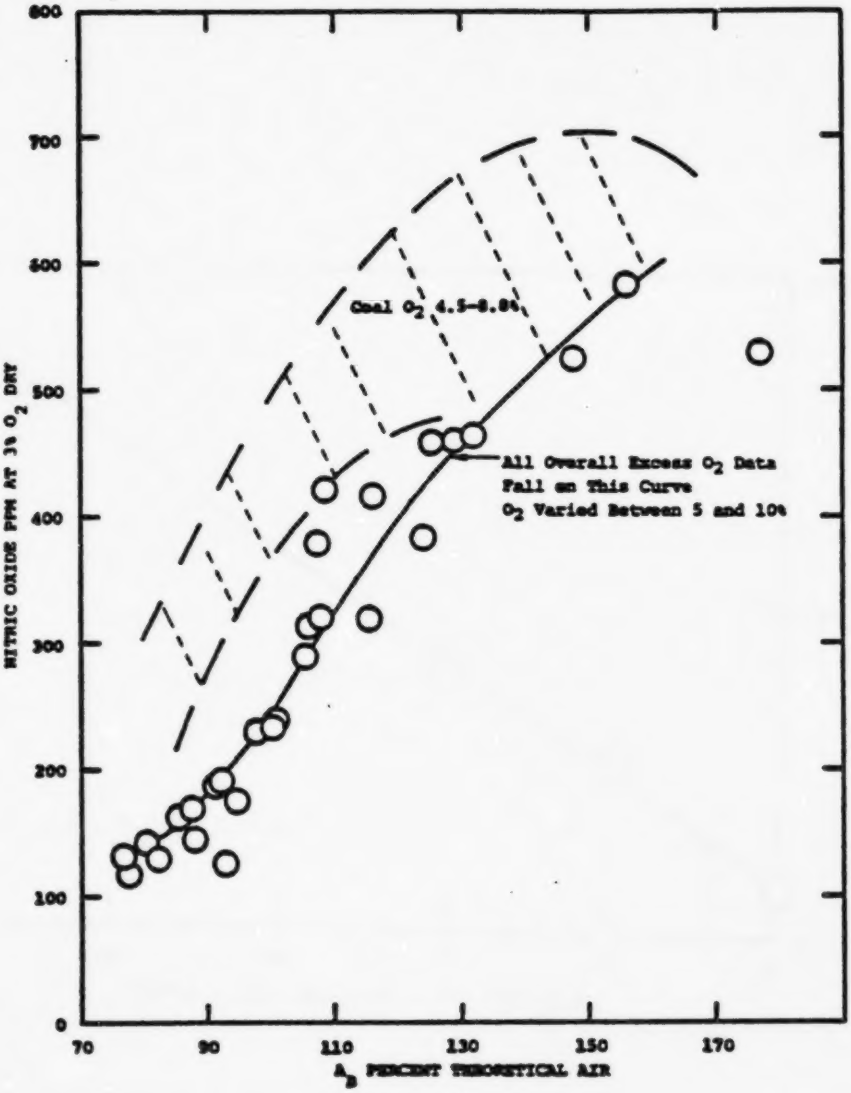


Figure 4-7. Effect of staged combustion on nitric oxide emissions. CEA RDF optimum fraction (50%).

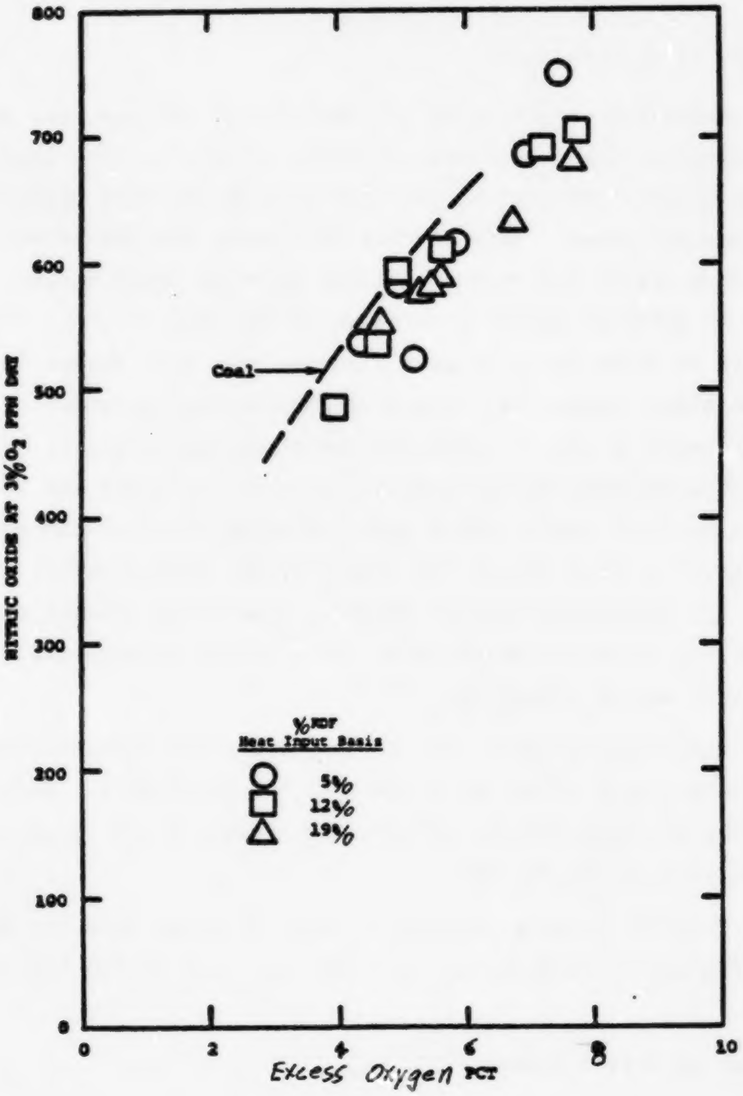


Figure 4-8. Effect of Americology RDF fraction on nitric oxide emissions. Single stage combustion.

B. Effect of Percent RDF--

The suspension co-firing of the Americology RDF and coal was difficult and not satisfactory for two primary reasons. First, at heat input rates for RDF exceeding about 10 percent of the total, it became very difficult to feed the RDF at constant rates. Much of this difficulty was traced to large pieces of plastic trash bag liners which would not shred to small sizes. These particles would catch on the flow surfaces of the feed system. This same material would at times melt inside the burner tube even though it was shielded from temperatures exceeding 367°K thus causing tube pluggage. In addition, moisture variations in the RDF affected the feeder performance. Second, was the poor suspension combustion characteristics of the paper and larger particles. This material would ignite upon discharge into the furnace but could be seen to travel past or all of the length of the boiler before settling to the floor of the combustion chamber where it then would smolder and ash. At heat input values above 10 percent RDF, the fraction of material settling to the boiler floor became excessive.

Co-firing this RDF with coal to 19 percent RDF produced less than 10 percent lower nitric oxide emissions than for coal alone. This reduction was essentially the same for all percent RDF between 5 and 19 percent. This effect can be seen in Figure 4-8.

The CO emissions were similar to those obtained with the CEA-RDF, typically 50-70 ppm and did not change over the range of RDF fractions evaluated.

C. Effect of Staged Combustion--

Staging of the combustion air when co-firing 12 percent RDF and the balance coal for various overall excess oxygen levels showed reductions in nitric oxide emissions up to approximately 50 percent. The absolute NO concentrations were between 0 and 29 percent lower than for coal only staged combustion. Unlike the CEA-RDF which showed an influence due to excess oxygen while staying, the Americology RDF nitric oxide emissions were not significantly influenced by the excess oxygen concentration. This effect is seen in Figure 4-9.

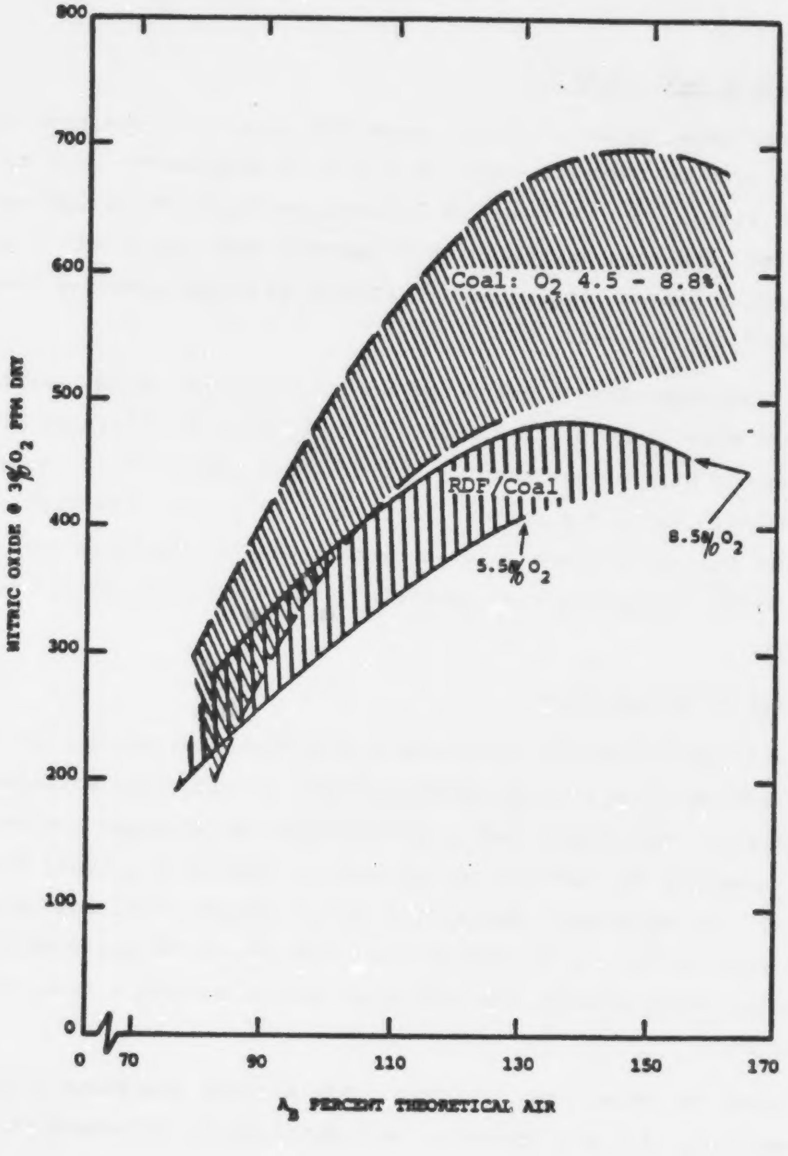


Figure 4-9. Effect of staged combustion on nitric oxide emissions. Americology RDF optimum fraction (12%, Heat Input Basis).

4.2.4 Hazardous Waste RDF/Coal

Two different types of liquid hazardous waste were co-fired with coal and tri-fired with coal and CEA-RDF. The initial experiments used benzene as the hazardous waste. The benzene was co-fired at 5 and 10 percent heat input ratios with coal and then tri-fired at 10 percent heat input with 6 and 36-percent CEA-RDF, balance coal. No operational problems occurred because of the addition of the benzene.

The final experiments using the second hazardous waste, waste lubricating oil, were more limited. The testing was limited to obtaining polycyclic samples using the high volume sampler train. Data was taken at 20 percent waste oil, balance coal; 9.4 percent waste oil, 40 percent CEA-RDF, balance coal; and 18.9 percent waste oil, 40.8 percent CEA-RDF, balance coal. As with the benzene tests, no operational problems were encountered due to the hazardous waste oil.

A. Effect of Excess Air--

It was found that the co-firing of the hazardous waste oils with coal produced essentially the same or slightly lower nitric oxide emissions than coal only firing. Since both test oils had very low nitrogen contents, the same argument as for the CEA-RDF can be made to explain why lower nitric oxide emissions were not obtained. Due to the higher oxygen availability of the coal stream when co-firing, higher nitric oxide emissions are produced by the coal combustion which offsets the reduction due to burning a fuel with lower nitrogen content.

As with the other previous tests, the minimum operating conditions, on set of CO emission, did not appear to be significantly different than for coal only combustion.

The influence of excess oxygen on the tri-firing tests was the same as for all previous tests.

B. Effect of Percent Waste Oil and Waste Oil Type--

There were apparent differences between the benzene and lubricating waste oil results. However, it should be noted that these apparent differences could be related to the coal fraction rather than the oil type. As discussed previously, it would be expected that the nitric oxide emissions would be reduced as the fraction of coal is reduced and the fraction of heat input is shifted toward the lower nitrogen fuel (CEA-RDF or waste oil). This effect would of course have to offset any increases due to the effect of higher oxygen availability in the coal combustion air, but from the trends seen for coal only nitric oxide emissions, the NO emissions above about 9 percent excess O_2 (~75 percent excess air) start to decrease. Thus, the two effects could start to become additive below about 60 percent coal fraction.

C. Effect of Staged Combustion--

A series of staged combustion tests were made with co-fired 10 percent benzene and 90 percent coal. The results showed little effect on any of the operation parameters or emissions. With the exception of a few data points at high excess air condition, all of the nitric oxide emissions were within the range measured for the coal only tests.

4.3 PARTICULATE LOADING AND SIZING

Flue gas particulate loading and sizing determination were made for a large number of test points. All sizing measurements were made using the MRI cascade type impactor. The loading measurements were made using either the standard EPA Method 5 train or the particulate catch from the high volume sample train. Thus, for those test points where POM/PCB samples were obtained, the particulate loading measurements were determined from the cyclone and filter used in the POM/PCB train. A summary of the loading and sizing is given in Table 4-1 for all test points where those measurements were made.

The particulate size values shown in Table 4-1 were taken from plots similar to Figure 4-10 which shows three of the test points. The values in Figure 4-1 are all in microns for the particle size at 50 percent cumulative weight (D_{50}). The size data does not show any significant trends other than a slightly larger particle size than for coal when either RDF is co-fired.

The particulate loadings show little difference in magnitude between coal only or co-fired conditions. The loadings do increase for coal only

TABLE 4-1. PARTICULATE LOADING AND SIZING SUMMARY

Test Point	Fuel Mixture (Pct HHV basis)	Calc. Ash* Loading ng/J	Measured Loading ng/J	Measured Mean Size D_{50}, μ
2	100% Coal	2.7×10^3	0.98×10^3	4.4
4	100% Coal Staged	2.7	1.53	5.1
6R	10% CEA, 90% Coal	3.17	1.36	--
8R	20% CEA, 80% Coal	3.79	1.50	--
10R	50% CEA, 50% Coal	5.30	1.38	--
13	50% CEA, 50% Coal	5.30	0.93	6.8
13R	50% CEA, 50% Coal	5.30	1.00	--
15	50% CEA, 50% Coal Staged	5.10	0.98	5.3
17	5% Americology, 95% Coal	3.01	0.90	--
19	12% Americology, 88% Coal	3.58	0.96	--
21	19% Americology, 81% Coal	3.97	0.87	--
24	12% Americology, 88% Coal Staged	3.58	1.00	5.2
26	12% Americology, 88% Coal Staged	3.58	1.12	5.7
30	10% Benzene, 90% Coal	2.55	0.94	4.7
32	6% CEA, 10% Benzene, 84% Coal	2.77	0.96	6.6
34	36% CEA, 10% Benzene, 54% Coal	4.39	0.86	7.3
34R	36% CEA, 10% Benzene, 54% Coal	4.39	1.06	--
36	100% Coal Staged	2.72	1.80	4.5
38	40% CEA, 9.4% Waste Oil, 50.6% Coal	4.62	1.05	10.0
39	20% Waste Oil, 80% Coal	2.02	0.90	8.2
40	40.8% CEA, 18.9% Waste Oil, 40.3% Coal	4.39	1.22	6.4

*Based on emission of all of the ash contained in the fuel.

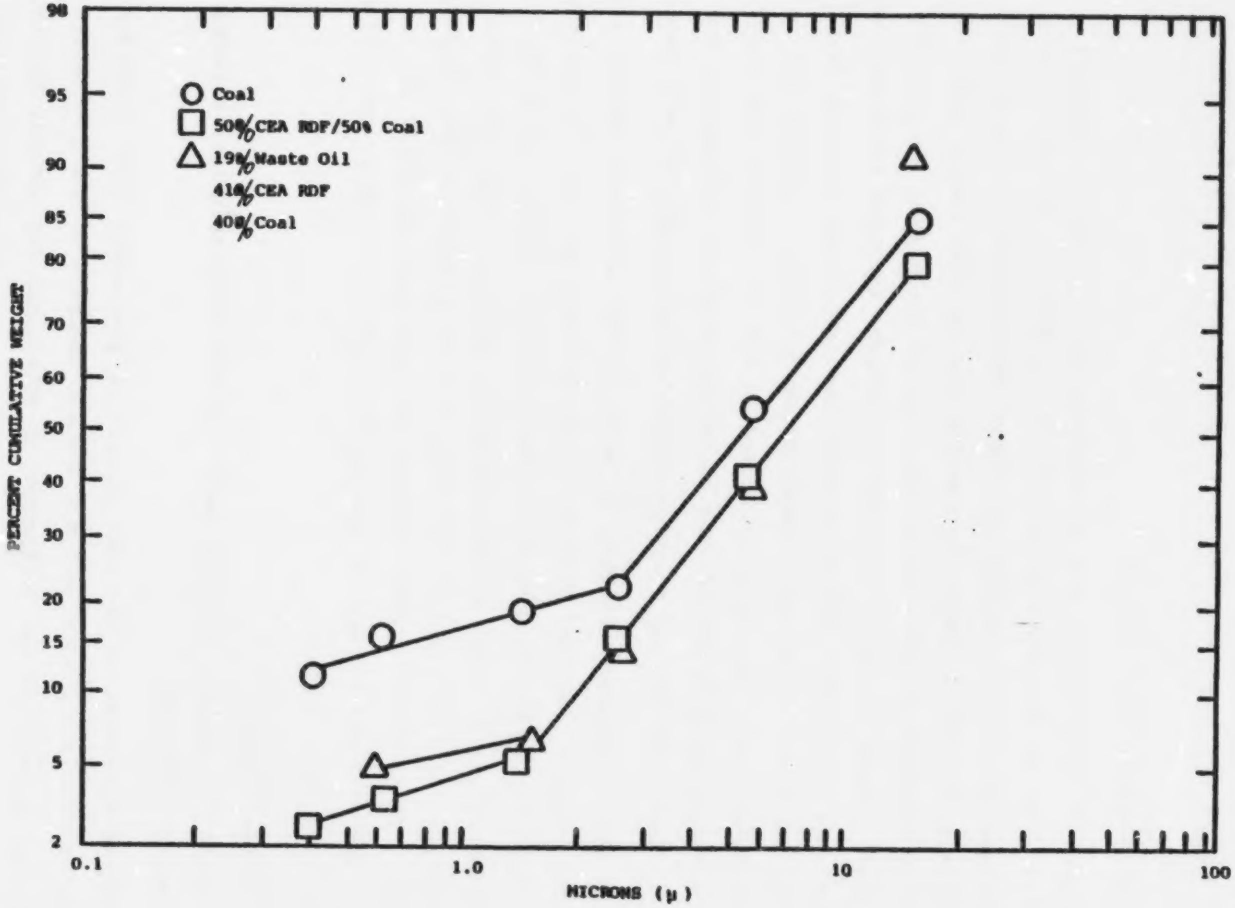


Figure 4-10. Typical particulate size distributions single stage combustion.

firing when staged combustion is used; this effect has been seen in oil firing experiments and is due to an increase in unburned carbon in the flue gas.

4.4 TRACE ELEMENTS AND COMPOUNDS

Samples of the flue gas were taken using the high volume sampling system (HVSS) train as described in Appendix B. A total of 15 samples were taken at various test matrix numbers for later possible trace element, inorganic and organic analysis. These test points and the test sample number identification assigned to these points is shown in Table 4-2. Particulate matter, filters, gases collected on a sorbent column, impinger solutions, and train rinses were collected. Twelve of these samples, along with two fuel samples, were submitted to Battelle Laboratories for Level 1 organic and inorganic analyses using the procedures cited in Ref. 6. Several additional analyses including analysis for organic chlorines, dioxins, polynuclear aromatic hydrocarbons (PAH's), and polychlorinated biphenyls (PCB's) were made.

From the 12 samples submitted to Battelle, the analytical emphasis was placed on the samples from test numbers 2, 15, 32, 34R, and 38. The analysis methods included spark source mass spectrometry (SSMS), atomic absorption spectrophotometry (AAS), total chromatographable organics (TCO), gravimetric organics (GRAV), infrared spectroscopy (IR), and low resolution mass spectrometry (LRMS). The list of samples and analyses performed are shown in Table 4-3. The complete results of the Battelle analytical study are included as Appendix C of this report.

4.4.1 Organic Analysis

Samples for organic analysis were extracted with methylene chloride per EPA Level 1 procedure.

Samples collected in the oven portion of the sample train (cyclone catches and particulate filter) did not require analysis of the volatiles since the oven temperature was sufficient to volatilize any species present. Those samples for which the total organic loading (volatiles plus nonvolatiles) exceeded 15 mg were fractionated by liquid chromatography (LC) using the fractions as listed in Table 4-4. This scheme yields seven fractions

TABLE 4-2. HVSS SAMPLE TEST POINTS

Test No.	Sample No.	Fuel Type and Btu Fraction
2	A	Coal
4	B	Coal (Staged Combustion)
13	C	50% CEA RDF/50% Coal
15	D	50% CEA RDF/50% Coal (Staged Combustion)
13R	E	50% CEA RDF/50% Coal
30	M	10% Benzene/90% Coal
34	N	36% CEA RDF/10% Benzene/54% Coal
32	O	6% CEA RDF/10% Benzene/84% Coal
24	P	12% Americology RDF/88% Coal
26	Q	12% Americology RDF/88% Coal (Staged Combustion)
36	R	Coal (Staged Combustion)
34R	S	36% CEA RDF/10% Benzene/54% Coal
38	1	9.4% Waste Oil/40% CEA RDF/50% Coal
39	2	20% Waste Oil/80% Coal
40	3	18.9% Waste Oil/40% CEA RDF/40.3% Coal

TABLE 4-3. LIST OF HVSS SAMPLES SELECTED FOR ANALYSIS AND ANALYSES PERFORMED

Test No.	Fuel Type	Extraction	GRAV(1) TCO* IR	SSMS(2)	AAS(3) (Hg)	AAS(3) (Sb, As)	LC-(4) IR-LRMS†
XAD-2 Sorbent Cartridge							
2	100% Coal	x	x	x	x		x
4	100% Coal	x	x	x	x		
13	50% CEA RDF/50% Coal	x	x	x	x		x
15	50% CEA RDF/50% Coal	x	x	x	x		x
13R	50% CEA RDF/50% Coal	x	x	x	x		x
30	10% Benzene/90% Coal	x	x				x
32	6% CEA RDF/10% Benzene/84% Coal	x	x				x
36	100% Coal	x	x				
34R	36% CEA RDF/10% Benzene/54% Coal	x	x				x
38	9.4% Waste Oil/40% CEA RDF/50.6% Coal	x	x				x
39	20% Waste Oil/80% Coal	x	x				
40	18.9% Waste Oil/40.8% CEA RDF/40.3% Coal	x	x				
Particulate Filters							
2	Coal	x	x	x	x		
4	Coal	x	x	x	x		
13	Coal	x	x	x	x		
15	Coal	x	x	x	x		
13R	Coal	x	x	x	x		
30	Coal	x	x	x	x		
32	Coal	x	x	x	x		
36	Coal	x	x	x	x		
34R	Coal	x	x	x	x		
38	Coal	x	x	x	x		
39	Coal	x	x	x	x		
40	Coal	x	x	x	x		
Cyclone Catch							
4	Coal	x	x	x	x		
13	Coal	x	x	x	x		
15	Coal	x	x	x	x		
13R	Coal	x	x	x	x		
30	Coal	x	x	x	x		
32	Coal	x	x	x	x		
36	Coal	x	x	x	x		
34R	Coal	x	x	x	x		
38	Coal	x	x	x	x		
39	Coal	x	x	x	x		
40	Coal	x	x	x	x		

(continued)

*Some samples were collected in the oven and due to the temperature, no volatiles are present.

†Only performed if minimum of 15 mg sample available.

(1)GRAV = gravimetric organics; TCO = total chromatographable organics; IR = infrared spectroscopy

(2)SSMS = spark source mass spectrometry

(3)AAS = atomic absorption spectrophotometry

(4)LC = liquid chromatography; LRMS = low resolution mass spectrometry

TABLE 4-3. (CONTINUED)

Test No.	Fuel Type	Extraction	GRAV[(1)] TCO* IR	SSMS[(2)]	AAS[(3)] (Hg)	AAS[(3)] (Sb, As)	LC-[(4)] IR-LRMS†
Organic Washes (Combined)							
2	Coal	x	x	x	x		x
4	Coal	x	x	x	x		
13	Coal	x	x	x	x		x
15	Coal	x	x	x	x		x
13R	Coal	x	x	x	x		x
30	Coal	x	x				
32	Coal	x	x				
36	Coal	x	x				
34R	Coal	x	x				
38	Coal		x				
39	Coal		x				
40	Coal		x				
First Impinger Solution							
2	Coal			x	x		
4	Coal			x	x		
13	Coal			x	x		
15	Coal			x	x		
13R	Coal			x	x		
30	Coal			x	x		
32	Coal			x	x		
36	Coal			x	x		
34R	Coal			x	x		
38	Coal			x	x		
39	Coal			x	x		
40	Coal			x	x		
Second and Third Impinger Solution							
2	Coal				x	x	
4	Coal				x	x	
13	Coal				x	x	
15	Coal				x	x	
13R	Coal				x	x	
30	Coal				x	x	
32	Coal				x	x	
36	Coal				x	x	
34R	Coal				x	x	
38	Coal				x	x	
39	Coal				x	x	
40	Coal				x	x	

*Some samples were collected in the oven and due to the temperature, no volatiles are present.

†Only performed if minimum of 15 mg sample available.

(1) GRAV = gravimetric organics; TCO = total chromatographable organics; IR = infrared spectroscopy

(2) SSMS = spark source mass spectrometry

(3) AAS = atomic absorption spectrophotometry

(4) LC = liquid chromatography; LRMS = low resolution mass spectrometry

TABLE 4-4. LIQUID CHROMATOGRAPHY ELUTION SEQUENCE

Fraction	Solvent Composition
1	Pentane
2	20 percent methylene chloride in pentane
3	50 percent methylene chloride in pentane
4	Methylene chloride
5	5 percent methanol in methylene chloride
6	20 percent methanol in methylene chloride
7	50 percent methanol in methylene chloride

which will contain the compound classes outlined in Table 4-5. All LC fractions were analyzed by gravimetry, gas chromatography for organic loading and infrared spectroscopy.

The results of this organic analyses are summarized in Tables 4-6, 4-7, and 4-8. The complete listing of all compounds found by the infrared analysis is given in Appendix C.

For the unfractionated samples, organic material was distributed in the normal manner. The majority of organic material was found in the XAD-2 and in the combined washes. Organics in the filter and cyclone catches were less by a factor of between 10 and 100. Somewhat surprising was that the sample having by far the most organic material was the combined washes from Test No. 2 (coal only). Had the XAD-2 from this run been highly loaded, it would appear that the sorbent had been overloaded causing the washes to have a high organic content. On the contrary, the XAD-2 from Test No. 13R (50 percent CEA RDF, 50 percent coal) had the most organics of any XAD-2 by a factor of 10. Thus, the origin of high organic loading in the Test No. 2 washes is unclear.

The distribution of organics in the fractionated material indicated that for the majority of samples most of the organic material was in Fraction 6, a highly polar fraction. This means that oxidized species such as ketones, amines and phenols account for a large part of these samples. Two samples varied from this trend: the XAD-2 extracts for Test No. 38 and 13R. Test No. 38, which burned 9.4 percent waste oil/40 percent CEA RDF/50 percent coal had 75 percent of the organics from XAD-2 in Fraction 3. From a health standpoint this would be of great interest as Fraction 3 can contain polynuclear aromatics (PNA's) and poly chlorinated biphenyls (PCB's). The XAD-2 from Test No. 13R (50 percent CEA RDF/50 percent coal) had organic material distributed as follows: 25 percent in Fraction 2, 32 percent in Fraction 3, and 27 percent in Fraction 6. This raises the same point as Run 1; that is, there is a significant amount of material in fractions which tend to contain PCB's and PNA's.

Infrared spectra obtained on each unfractionated organic sample gave information concerning the composition of these samples. Many components were

TABLE 4-5. DISTRIBUTION OF COMPOUND CLASSES IN LIQUID CHROMATOGRAPHIC FRACTIONS OF ORGANIC EXTRACTS

Fraction	Compound Class
1	Aliphatic hydrocarbons Halogenated aliphatics
2,3	Aromatic hydrocarbons Halogenated aromatics (PCB's)
4,5	Nonpolar oxygen or nitrogen containing species
6,7	Polar compounds - phenols, alcohols, amines, etc.

TABLE 4-6. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSIS

Analysis Summary

Fuel Type and Btu Fraction	XAD-2 mg/sample	Particulate Filter mg/sample	Cyclone Catch mg/sample	Organic Washes mg/sample	Total mg	Total mg/Btu
Coal	29.7	1.4	--	1663.1	1694.2	0.000451
Coal (Staged Combustion)	15.6	0.6	1.7	6.1	24.0	0.000006
50% CEA RDF/50% Coal	23.3	0.7	1.5	17.0	42.5	0.000011
50% CEA RDF/50% Coal (Staged Combustion)	46.0	1.0	1.1	21.0	69.1	0.000018
50% CEA RDF/50% Coal	122.0	0.9	1.2	13.0	137.1	0.000037
10% Benzene/90% Coal	35.0	0.2	0.9	--	36.1	0.000010
6% CEA RDF/10% Benzene/84% Coal	41.0	0.4	0.1	--	41.5	0.000011
Coal (Staged Combustion)	25.0	0.4	0.3	--	25.7	0.000007
36% CEA RDF/10% Benzene/54% Coal	39.0	0.5	0.2	--	39.7	0.000011
9.4% Waste Oil/40% CEA RDF/50% Coal	61.0	0.6	0.4	--	62.0	0.000017
20% Waste Oil/80% Coal	19.0	0.2	0.1	--	19.3	0.000005
18.9% Waste Oil/40% CEA RDF/40.3% Coal	19.0	0.4	0.2	--	19.7	0.000005

TABLE 4-7. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTIONS OF COMBINED WASHES AND XAD-2 CARTRIDGES

Fuel Type and Btu Fraction		Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
Coal	XAD-2	5.7	24.0	29.7
	Combined Wash	254.3	1408.8	1663.1
Coal (Staged Combustion)	XAD-2	3.6	12.0	15.6
	Combined Wash	--	6.1	--
50% CEA RDF/50% Coal	XAD-2	5.3	18.0	23.3
	Combined Wash	15.0	17.0	32.0
50% CEA RDF/50% Coal (Staged Combustion)	XAD-2	21.0	25.0	46.0
	Combined Wash	1.7	21.3	23.0
50% CEA RDF/50% Coal	XAD-2	94.0	28.0	122.0
	Combined Wash	19.1	12.4	31.5
10% Benzene/90% Coal	XAD-2	10.0	25.0	35.0
	Combined Wash	--	--	--
6% CEA RDF/10% Benzene/84% Coal	XAD-2	12.0	29.0	41.0
	Combined Wash	--	--	--
Coal (Staged Combustion)	XAD-2	7.0	18.0	25.0
	Combined Wash	--	--	--
36% CEA RDF/10% Benzene/54% Coal	XAD-2	10.0	29.0	39.0
	Combined Wash	--	--	--
9.4% Waste Oil/40% CEA RDF/50% Coal	XAD-2	19.0	42.0	61.0
	Combined Wash	--	--	--
20% Waste Oil/80% Coal	XAD-2	6.0	13.0	19.0
	Combined Wash	--	--	--
18.9% Waste Oil/40% CEA RDF/40.3% Coal	XAD-2	5.0	14.0	19.0
	Combined Wash	--	--	--

TABLE 4-8. LOW RESOLUTION MASS SPECTROMETRY RESULTS FOR SELECTED LIQUID CHROMATOGRAPHY FRACTIONS

Sample	Fraction #	Intensity	Interpretation
Combined washes	2 and 3	100	Phthalates
Test No. 2		5	Aromatic amine
Coal		30	Carboxylate
	4	100	Phthalates
		20	Fused ring compounds
	5	100	Phthalates
		15	Fused ring compounds
	6 and 7	100	Phthalates
		10	Alcohol
XAD-2 extract	6 and 7	100	Carboxylates
Test No. 2		25	Phthalates
Coal		25	Amine
		20	Benzoic acid
Combined washes	6 and 7	100	Carboxylates
Test No. 13		40	Methyl esters
50% CEA RDF/50% Coal		25	Phthalates
		15	Aromatic amines
XAD-2 extract	6 and 7	100	Carboxylates
Test No. 13		30	Phthalates
50% CEA RDF/50% Coal		30	Benzoic acid
		15	Aromatic amines

those expected from any combustion source: carboxylic acids, other carbonyl containing compounds, aliphatic hydrocarbons, and anhydride. In addition, several of the combined washes contained inorganic nitrate. Two components seen were suspected to be contaminants: silicone (a common lubricant) and tri cresyl phosphate (a plasticizer).

4.4.2 Inorganic Analysis

Cyclone catches, particulate filters, XAD-2 cartridges, and impinger solutions were analyzed for elements lithium through uranium by spark source mass spectrometry (SSMS). A summary of several of the more important elements found is given in Table 4- 9. A complete listing of all elements is found in Appendix C.

These same samples were also analyzed for mercury (Hg) by atomic absorption spectrophotometry (AAS). In addition, combined second and third impinger solutions were analyzed by AAS for antimony (Sb) and arsenic (As). These results are given in Tables 4-10 and 4-11.

The SSMS results showed about half the samples had low levels of lead. The AAS results showed that the XAD-2 cartridge had more mercury than the other types of samples (filters, particulates, impinger solutions). The XAD-2 sample from Test 13R had the most mercury of the XAD-2's by a factor of 10. Test 13R was with 50 percent CEA RDF/50 percent coal, the CEA RDF had higher levels of mercury than the coal so this result is not unsuspected. Antimony was not detected in any sample. Arsenic was very low or not detected.

4.4.3 Polynuclear Aromatic Hydrocarbons (PAH)

The organic extracts of the particulate filters were first screened for PAH's by a fluorescence spot test. Results are given in Table 4-12. This spot test is explained more fully in Ref. 7. The technique is based on the sensitization of the inherent fluorescence of PAH's and can routinely detect compounds present at the 10 pg level. Accuracy is reported within one order of magnitude.

Only two samples were positive for PAH using this spot test: filter extracts from test numbers 38 and 40 at a level of 10^{-3} g/l. It was decided

TABLE 4-9. SSMS RESULTS FOR INORGANIC ELEMENTS
Highest Concentration Elements Found
µg/Btu

Fuel Type	Coal	Coal Staged	50 CEA 50 Coal	50 CEA 50 Coal Staged	50 CEA 50 Coal	10 Benzene 90 Coal	6 CEA 10 Benzene 84 Coal	Coal Staged	36 CEA 10 Benzene 54 Coal	9.4 Oil 40 CEA 50 Coal	20 Oil 80 Coal	18.9 Oil 40 CEA 40.3 Coal
Hg	0.00287	0.00292	0.02573	0.00294	0.00294	0.00007	0.00007	0.00011	0.00007	0.00007	0.00006	0.00006
Cu	0.00654	0.01237	0.00334	0.00272	0.00263	0.000553	0.00105	0.00048	0.00069	0.00247	0.00097	0.00182
Ni	0.01305	0.00943	0.00946	0.01745	0.01125	0.00209	0.00216	0.001086	0.00212	0.00233	0.00373	0.00182
Fe	0.42172	0.31127	0.3950	0.64509	0.46839	0.30557	0.30984	0.39815	0.52269	1.10941	0.91162	0.45050
Ti	0.29271	0.05969	0.06188	0.07161	0.07846	0.11859	0.08215	0.03619	0.08392	0.13341	0.18143	0.10489
Ca	0.18044	0.02825	0.05165	0.04832	0.06647	0.01594	0.03112	0.00505	0.03533	0.19843	0.02735	0.05255
K	0.00335	0.00241	0.00099	0.00031	0.00140	0.00003	—	0.00006	0.00003	0.00009	0.00003	0.00018
S	1.6523	3.1440	2.4541	1.7003	1.2690	0.00419	0.00505	0.00531	0.00628	0.00537	0.00158	0.02223
Si	2.9334	4.0452	3.79451	2.9257	2.8830	2.7073	0.43270	0.58925	1.45854	1.54329	1.26572	0.61974
Al	4.1925	4.3250	2.7172	2.1043	3.0727	3.8760	1.03764	3.74016	3.12908	3.30043	2.71243	0.89384
Mg	0.02175	0.07572	0.11206	0.21193	0.05262	0.04953	0.05188	0.02051	0.10737	0.05617	0.01494	0.09082
Na	0.04262	0.11450	0.78816	1.5624	0.26100	0.01873	0.22268	0.01425	0.64419	0.25108	0.01155	0.30465

*Particulate filter and cyclone catch only.

TABLE 4-10. AAS RESULTS FOR MERCURY

Fuel Type and Btu Fraction	MERCURY µG/SAMPLE							
	XAD-2	Particulate Filter	>3 µ Particulate Cyclones	Organic Rinse and Extracted Condensate	1st Impinger Solutions	2nd & 3rd Solutions	Total µg	µg/kJ
Coal	21	3.7	--	5.4	5.3	5.7	41.1	0.000010
Coal (Staged Combustion)	9	28.0	24.0	0.8	0.7	0.1	62.6	0.000015
50% CEA RDF/50% Coal	95	9.1	17.0	<0.1	5.5	13.0	139.7	0.000035
50% CEA RDF/50% Coal (Staged Combustion)	10	180.0	220.0	0.5	1.4	0.2	412.1	0.000104
50% CEA RDF/50% Coal	400	7.6	34.0	1.8	4.3	0.6	448.3	0.000113
10% Benzene/90% Coal	--	3.1	6.1	--	3.5	16.0	--	--
6% CEA RDF/10% Benzene/84% Coal	--	2.2	16.0	--	2.8	6.5	--	--
Coal (Staged Combustion)	--	15.0	20.0	--	0.7	4.0	--	--
36% CEA RDF/10% Benzene/54% Coal	--	2.6	66.0	--	2.0	<0.7	--	--
9.4% Waste Oil/40% CEA RDF/50% Coal	--	5.1	56.0	--	0.7	3.0	--	--
20% Waste Oil/80% Coal	--	0.6	<20.0	--	0.5	1.1	--	--
18.9% Waste Oil/40% CEA RDF/40.3% Coal	--	11.0	76.0	--	0.8	1.3	--	--

TABLE 4-11. AAS ANALYSIS FOR MERCURY, ARSENIC, AND ANTIMONY ON SECOND AND THIRD IMPINGER SOLUTIONS (COMBINED)

Fuel Type and Btu Fraction	Mercury µg/gr	Arsenic µg/gr	Antimony µg/gr
Coal	0.00588	<0.0004	<0.01
Coal (Staged Combustion)	0.00001	<0.0004	<0.01
50% CEA RDF/50% Coal	0.013402	<0.0004	<0.01
50% CEA RDF/50% Coal(Staged Combustion)	0.002105	<0.0004	<0.01
50% CEA RDF/50% Coal	0.00068	<0.0004	<0.01
10% Benzene/90% Coal	0.01798	<0.0004	<0.01
6% CEA RDF/10% Benzene/84% Coal	0.00817	<0.0004	<0.01
Coal (Staged Combustion)	0.00611	<0.0004	<0.01
36% CEA RDF/10% Benzene/54% Coal	0.00078	<0.0004	<0.01
9.4% Waste Oil/40% CEA RDF/50% Coal	0.00333	<0.0004	<0.01
20% Waste Oil/80% Coal	0.001158	<0.0004	<0.01
18.9% Waste Oil/40% CEA RDF/40.3% Coal	0.00146	<0.0004	<0.01

TABLE 4-12. RESULTS OF PAH SPOT TESTS ON PARTICULATE FILTER EXTRACTS

Fuel Type (Heat Input Basis)	POM Concentration (g/ℓ)
Coal	$<10^{-6}$
Coal (Staged Combustion)	$<10^{-6}$
50% CEA RDF/50% Coal	$<10^{-6}$
50% CEA RDF/50% Coal (Staged Combustion)	$<10^{-6}$
50% CEA RDF/50% Coal	$<10^{-6}$
10% Benzene/90% Coal	$<10^{-6}$
6% CEA RDF/10% Benzene/84% Coal	$<10^{-6}$
Coal (Staged Combustion)	$<10^{-6}$
36% CEA RDF/10% Benzene/54% Coal	$<10^{-6}$
9.4% Waste Oil/40% CEA RDF/50% Coal	$<10^{-3}$
20% Waste Oil/80% Coal	$<10^{-6}$
18.9% Waste Oil/40% CEA RDF/40.3% Coal	$<10^{-3}$

to run the filter extracts from test numbers 32 and 34R as well, even though the spot test did not show any PAH present. This decision was based on the fact that doing four PAH analyses was very little more work than two due to extensive calibrations needed.

These four samples were quantitatively analyzed for PAH's by electron impact gas chromatography/mass spectrometry (GS/MS). The results are given in Table 4-13.

4.4.4 PCB and Dioxin Analyses

Organic extracts were analyzed for total organic chlorine content. The samples were screened for PCB's using a GC with a Hall electrolytic conductivity detector. The results are shown in Table 4-14.

The original criterion for PCB and dioxin analysis was that any extract of the particulate which exceeded 58 $\mu g/m^3$ at the source would be analyzed for dioxins and PCB compounds. No particulate filter extracts exceeded this number. There was a further criterion stating that any of these samples exceeding 500 $\mu g/m^3$ of PCB's would be analyzed for PCB species. No sample approached this level of PCB concentration.

Because the XAD-2 extracts consistently showed organic chlorines, three were analyzed by high resolution GC/MS. Results, which were all negative, are shown in Table 4-15.

TABLE 4-13. PAH ANALYSIS OF XAD-2 EXTRACTS OF SELECTED RUNS

Compound	9.4% Waste Oil/ 40% CEA RDF/ 50% Coal (µg/sample)	18.9% Waste Oil/ 40% CEA RDF/ 40.3% Coal (µg/sample)	36% CEA RDF/ 10% Benzene/ 54% Coal (µg/sample)	6% CEA RDF/ 10% Benzene/ 84% Coal (µg/sample)
Naphthalene	4	2	<0.5	0.5
Acenaphthene	3	<0.5	<0.5	<0.5
Phenanthrene	<0.5	3	<0.5	<0.5
Fluoranthene	3	<0.5	<0.5	<0.5
Chyrsene	3	8	<0.5	<0.5
Benzofluoranthene	15	24	<0.5	<0.5
Benzo(e)pyrene	0.7	2	<0.5	<0.5
Indeno(1,2,3-c,d)pyrene	2	8	<0.5	<0.5
Benzo(g,h,i)pyrene	14	<0.5	<0.5	<0.5
Coronene	16	13	<0.5	<0.5

Detection Limit 0.5 µg

TABLE 4-14. GAS CHROMATOGRAPHY ANALYSIS FOR ORGANIC CHLORINE

Fuel Type and Btu Fraction	XAD-2 <------	Particulate Filters ------	Cyclone Catch μg/m^3 ------	Organic Washes ------>
Coal	5	ND*	--	--
Coal (Staged Combustion)	5	ND	ND	12
50% CEA RDF/50% Coal	--	ND	--	--
50% CEA RDF/50% Coal (Staged Combustion)	27	ND	0.1	13
50% CEA RDF/50% Coal	34	ND	ND	26
10% Benzene/90% Coal	6	ND	0.1	--
6% CEA RDF/10% Benzene/84% Coal	9	ND	ND	5
Coal (Staged Combustion)	5	ND	ND	--
36% CEA RDF/10% Benzene/54% Coal	5	ND	ND	0.7
9.4% Waste Oil/40% CEA RDF/50% Coal	7	ND	0.6	1
20% Waste Oil/80% Coal	6	ND	ND	--
18.9% Waste Oil/40% CEA RDF/40.3% Coal	4	ND	ND	--

*ND = Not Detected

TABLE 4-15. RESULTS OF HRGC/HRMS ANALYSES FOR 2, 3, 7, 8-TETRACHLORODIBENZO-p-DIOXIN IN XAD-2 EXTRACTS

	Amount of TCDD Present in Sample, pg	% Recovery of ^{13}C-Labeled TCDD Internal Standard
6% CEA RDF/10% Benzene/84% Coal	<2.0	97
9.4% Waste Oil/40% CEA RDF/50% Coal	<3.1	40
36% CEA RDF/10% Benzene/54% Coal	<1.5	65

REFERENCES

1. l'Breque, M., "Garbage - Refuse or Resource," Popular Science, p. 75, June 1977.

2. "Power from Waste - A Special Report," Power Magazine, pp. S2-S-24, February 1975.

3. Hollander, H. I., "Combustion Factors for Utilizing Refuse Derived Fuels in Existing Boilers," presented at the Fourth National Conference on Energy and the Environment, Cincinnati, OH, October 4-7, 1976.

4. Quan, V. et al., Analytic Scaling of Flow Field and Nitric Oxide in Combustors, Paper presented at the EPA Pulverized Coal Combustion Seminar, June 1973.

5. Busch, C. F. et al., Co-firing of Four Refuse Derived Fuels in a Pilot-Scale Facility, EPA Contract 68-02-1885, March 1978.

6. IERL-RTP Procedures Manual Level 1 Environmental Assessment (Second Edition), EPA 600-7-78-201, October 1978.

7. Smith, E. M. and Levins, P. L., Sensitized Fluorescence for the Detection of Polycyclic Aromatic Hydrocarbons, EPA 600/70780182, September 1978.

APPENDIX A

DETAILED DESCRIPTION OF COAL FIRING EQUIPMENT

The KVB combustion research laboratory is designed to fire a wide variety of gaseous, liquid, and solid fuels including conventional fossil fuels and a large number of unconventional fuels. This latter category has included not only the refuse-derived materials but also other substances such as coal-derived liquids, gasifier char, waste lubricants, pyrolytic oil derived from various sources, oil-water emulsions, and coal-oil slurries.

The system in which these fuels can be evaluated has as its base an 780 kW boiler shell. In conjunction with this boiler several flow arrangements can be established for firing various fuels. The flow arrangement used for this program is shown in Figure A-1.

There are five major groups of components which, when used in conjunction with each other, allow simulation of a variety of industrial and utility boiler applications. The following paragraphs describe each major component in detail.

COMBUSTION AIR AND FLUE GAS

Combustion air is drawn into the system by a low pressure centrifugal blower with a static pressure of 5 cm H_2O at 1589 kg of air flow/hour. The air is discharged into a plenum where recirculated flue gas can also be added by a high-pressure/high-temperature centrifugal blower having a static pressure of 7.7 K Pa H_2O at 1634 kg of air flow/hour.

The combustion air leaves this plenum through a 100-tube air-to-air heat exchanger where the temperature of the combustion air can be raised to 644°F when required. The heat exchanger is fired by an automatic gas-fired burner operating at pressures lower than the combustion air, and any air leakage which might occur is toward the air preheater burner, thus preventing vitiation of the combustion air.

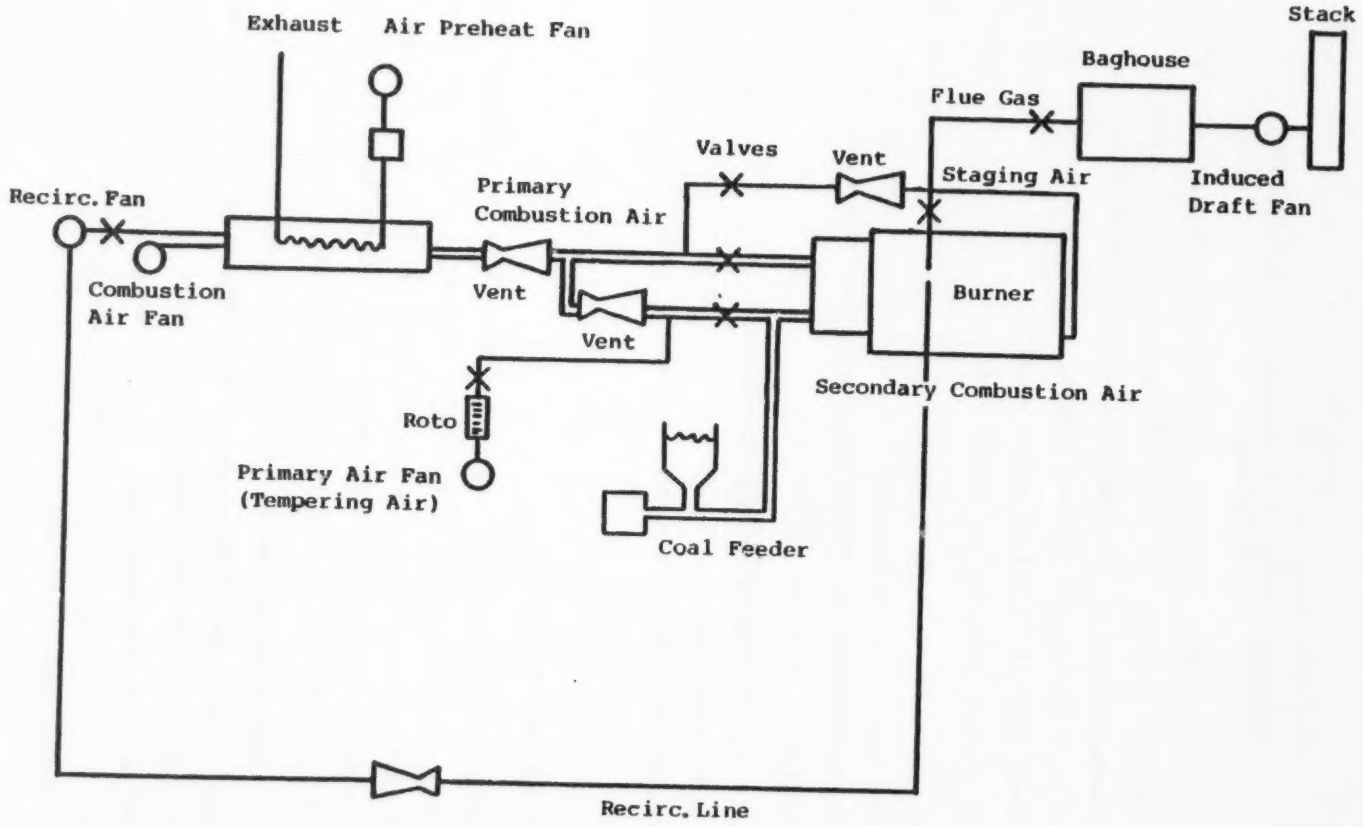

Exhaust
Air Preheat Fan
Stack
Baghouse
Flue Gas
Valves
Vent
Staging Air
Induced
Draft Fan
Recirc. Fan
Primary
Combustion Air
Combustion
Air Fan
Vent
Burner
Vent
Secondary Combustion Air
Roto
Primary Air Fan
(Tempering Air)
Coal Feeder
Recirc. Line

Figure A-1. Eighty-horsepower flow schematic for solid fuel evaluations.

The air mass flow is measured downstream of the heat exchanger by a calibrated venturi, accounting for any leakage which might have occurred through the preheater.

The combustion air from the air heat exchanger is split into two streams after the flow venturi to form what is normally called secondary air and primary air on a suspension fired coal boiler.

The primary air stream is passed through a calibrated venturi after which it is cooled by the addition of metered tempering air which is supplied from a high pressure centrifugal blower having a static pressure of 9.0 K Pa at 84.4 kg of air flow/hour. The combined primary air stream then is used to carry the pre-pulverized coal to the burner.

The secondary combustion air can be split into two streams to allow staged combustion evaluations. This is accomplished with two valves located just upstream of the burner windbox. One valve adjusts burner flow and upstream pressure; the other adjusts staged air flow and upstream pressure.

When used, the staging air passes through a calibrated venturi and then to a torus located inside the boiler combustion chamber. The air is injected radially from the torus toward the axis of the combustion chamber through 32 orifices, each 1.43 cm in diameter.

Under normal combustion, all of the secondary combustion air is supplied to the burner through a duct which is split into two ducts which enter the windbox from opposite sides. Perforated baffle plates in the windbox keep the air from passing directly to the nearest register vane and make its flow through the air registers uniform.

The combustion air passes through the burner where fuel is added and ignited. Combustion is completed in the boiler combustion chamber; the flue gas is exhausted from the boiler fire tubes into a plenum at the base of the exhaust stack.

Flue gas recirculation flow is drawn from this plenum when required; a damper is located at the outlet of the plenum to allow flow-pressure balancing of the system as needed.

Under normal operation the plenum damper is open, and boiler back pressure is maintained by a damper at the inlet to the baghouse. The baghouse is not normally required for oil operation. However, this facility also has the capability to fire solid fuels. Therefore, the flue gas is filtered through the baghouse before being drawn into the exhaust stack by a high-volume, low-pressure exhaust blower.

FUEL SYSTEM

The solid fuel burner is capable of burning subbituminous and bituminous coal as well as some chars. Other solid fuels have not been tested in the unit. In order to fire these fuels, it has been necessary to pulverize the solid fuels to a fineness normally stated for full size suspension systems which is nominally 70-80 percent through a 200-mesh screen.

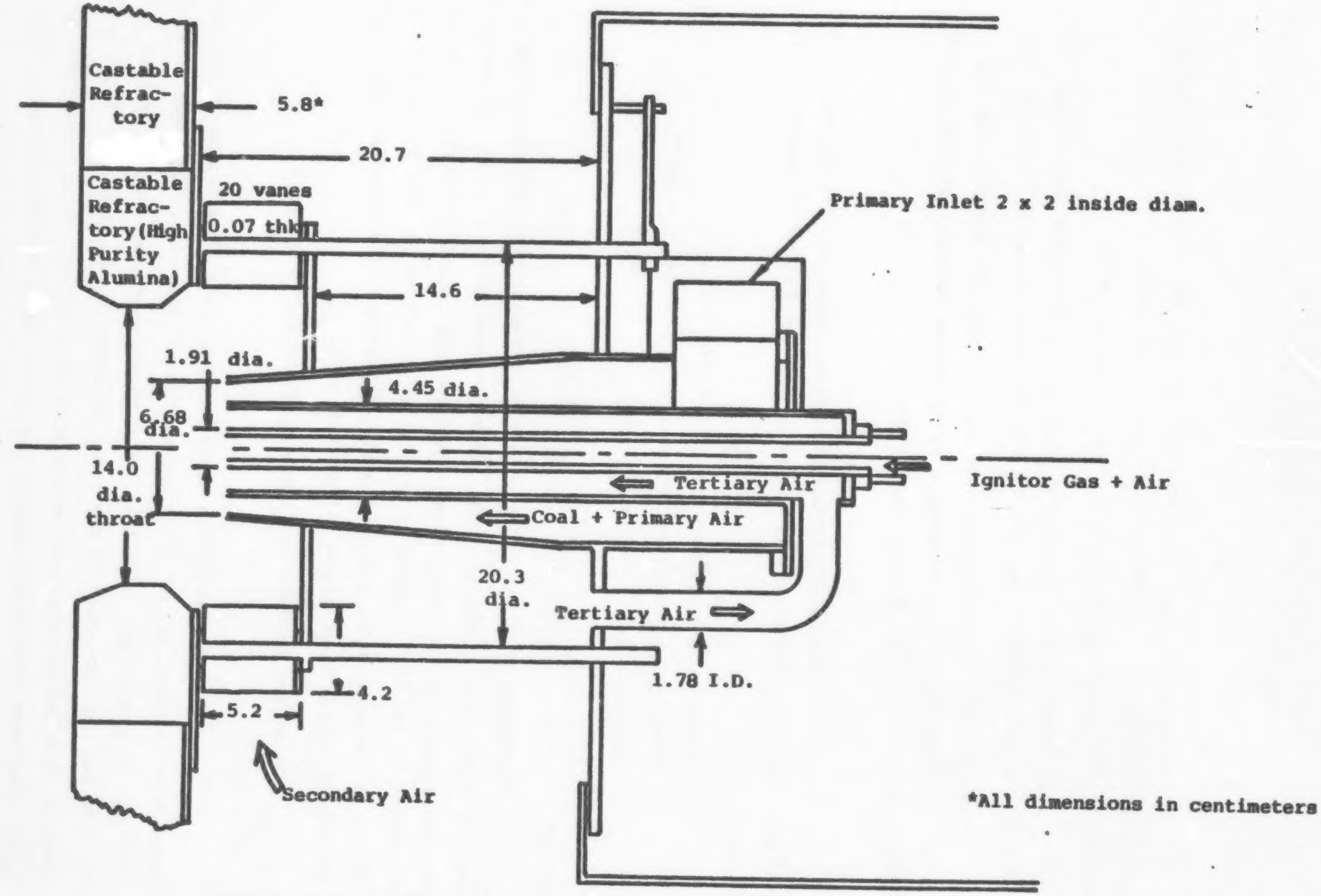
The solid fuels are pre-pulverized to the required specifications off-site, placed in 23 kg plastic bags and then transported to the combustion facility in 208 liter drums.

The method of feeding the pulverized solids to the primary air stream is a vibratory feeder. This feeder (Vibrascrew) has a 0.23 cubic meter line bin hopper coupled to a 3.8 cm diameter screw. The feed capacity of this system is approximately 136 kg/hr of 641 kg/m^3 density material.

BURNER

The burner used is a scaled down version of a modern coal-fired utility boiler burner. The modeling approach used was to preserve the temperature, velocities and volumetric heat release rate of the full size unit as well as geometric similarity of the burner. The scaled down version of the full size burner is shown schematically in Figure A-2.

This burner has a 16-vane variable-vane-angle air register used for imparting swirl to the air flow. Each vane is independently variable so as to permit positive identification of vane position.


Castable Refractory
5.8*
20.7
Castable Refractory (High Purity Alumina)
20 vanes
0.07 thk
Primary Inlet 2 x 2 inside diam.
14.6
1.91 dia.
4.45 dia.
6.68 dia.
14.0 dia. throat
Ignitor Gas + Air
Tertiary Air
Coal + Primary Air
20.3 dia.
Tertiary Air
1.78 I.D.
4.2
5.2
Secondary Air

*All dimensions in centimeters

Figure A-2. Small-scale version of a full-size coal burner.

Ignition is provided by a premixed gas igniter with a high voltage spark at the discharge of the ignition tube. The ignition is fixed and located on the burner centerline as shown in Figure A-2.

Just downstream of the burner throat is a diverging quarl cast from high-alumina refractory. The contour for the quarl is given in Figure A-2.

The primary combustion air and coal mixture are brought into the burner tangentially. This produces a fixed degree of swirl exiting from the primary flow path at the exit of the burner.

The solids fuel facility has been fired using various degrees of air preheat. Normally the system is operated with the following combustion air temperatures:

Secondary air delivered to the burner	561°K
Mixed primary air/coal stream	340°K - 367°K
Tempering air	328°K

BOILER

The boiler shell is a Scotch marine dry-back type originally designed for low combustion intensity. The steam produced by this boiler is vented at one atmosphere. At a firing rate of 880 kW, the boiler's volumetric firing intensity is 398 kW/m^3, which is typical of oil-fired utility boilers. The boiler is operated under a slight positive pressure controlled by the stack dampers to insure true excess air measurements.

The boiler schematic is shown in Figures A-3 and A-4.

The boiler has 64 5.1-cm-diameter fire tubes in addition to the main combustion chamber, all of which are surrounded by water. In order to minimize the very cold wall effect in the combustion chamber, a set of heat shields has been attached to the inner diameter of the chamber. These shields operate at a temperature more nearly that of a typical water tube steam generator, thus more closely simulating the environment of such a boiler. The panels are removable for tests not requiring this type of simulation.

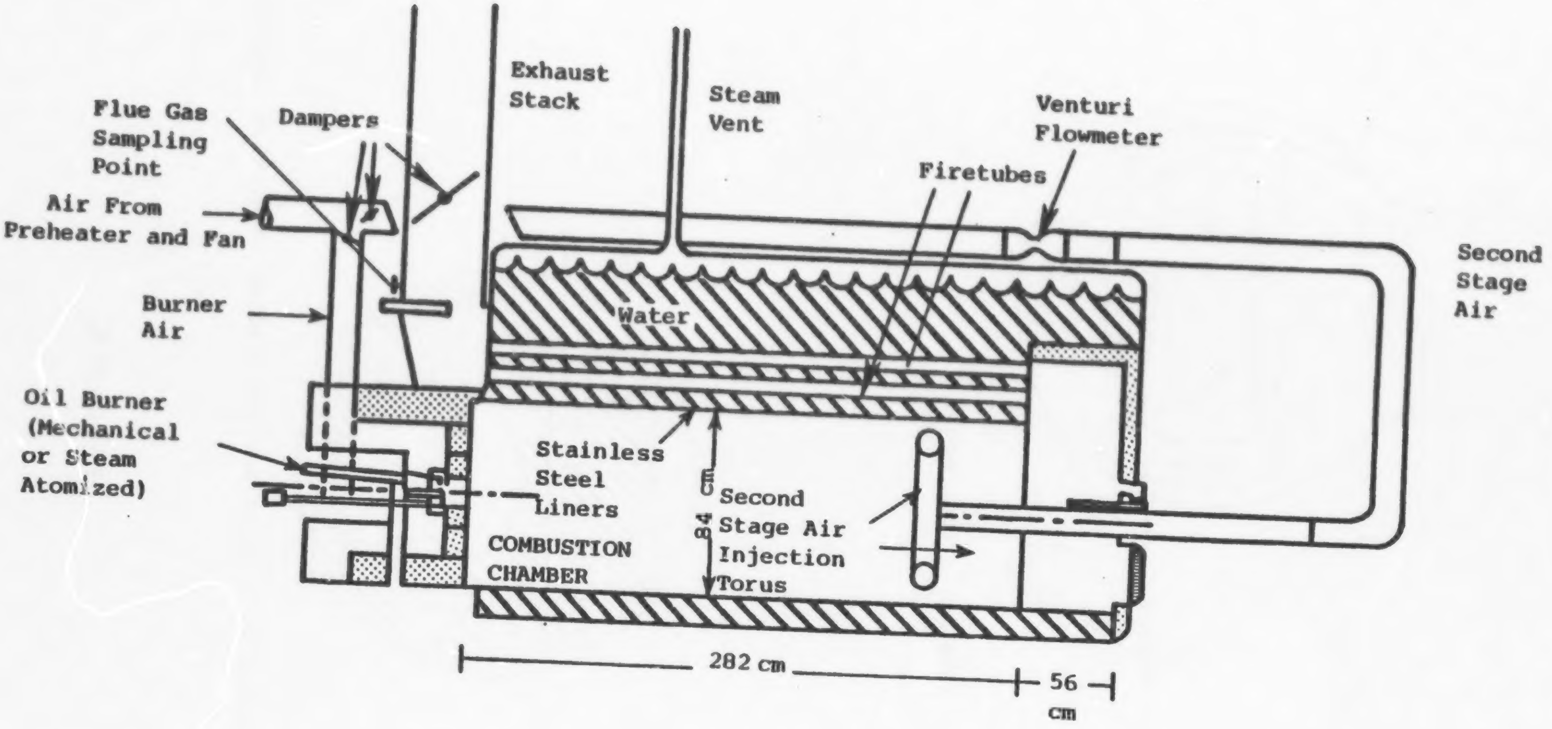

Flue Gas
Sampling
Point
Dampers
Exhaust
Stack
Steam
Vent
Venturi
Flowmeter
Firetubes
Air From
Preheater and Fan
Burner
Air
Water
Second
Stage
Air
Oil Burner
(Mechanical
or Steam
Atomized)
Stainless
Steel
Liners
84 cm
Second
Stage Air
Injection
Torus
COMBUSTION
CHAMBER
282 cm
56
cm

Figure A-3. Boiler Schematic

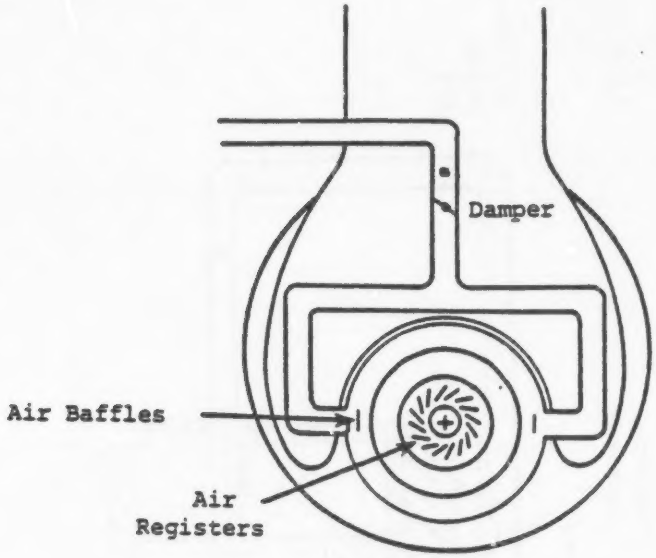

Damper
Air Baffles
Air
Registers

Figure 5a. Cross section through windbox.

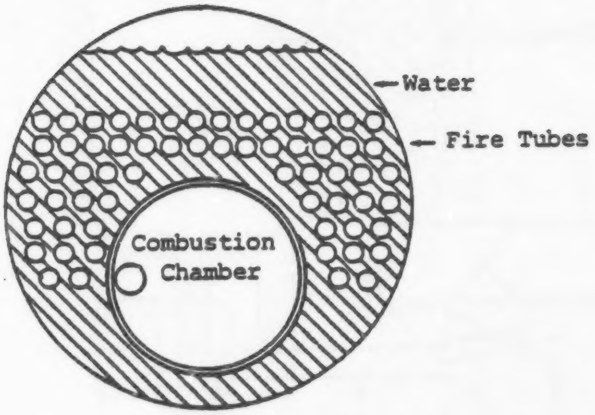

Water
Fire Tubes
Combustion
Chamber

Figure 5b. Cross section through combustion chamber.

Figure A-4.

Another benefit from the shields is that they minimize quenching of the combustion gases, thus reducing smoke and carbon monoxide emissions. This is most important for staged combustion operation which is used to demonstrate nitric oxide emission reductions.

The staging air is brought into the combustion chamber through a torus located approximately two-thirds the length of the combustion chamber from the burner. This torus has 32 orifices, each 1.43 cm in diameter, located on the inner diameter of the ring such that air is injected radially toward the center of the combustion chamber. The axial location of the ring can be varied for study of the location of the staged air during the combustion process.

The exhaust stack is sized for developing velocities during the test work which can be easily matched with the sampling equipment for isokinetic sampling.

INSTRUMENTATION

A complete instrument console houses all the various continuous gas monitors and recorders normally used to operate the combustion facility.

All temperature measurements are made with chromel-alumel thermocouples using digital readouts. All pressure measurements for the flow venturis, windbox, and stack pressures are made using water manometers. Higher pressures, such as fuel or steam pressures, are measured with bourdon gages.

Emissions instrumentation is extensive, providing measurement of all the criteria pollutants. Dry-basis concentrations of NO, O_2, CO, and CO_2 are measured continuously using a Thermo Electron Corporation chemiluminescent nitric oxide analyzer, a Beckman Model 742 oxygen electrolytic analyzer, a Horiba Model PIR2000 nondispersive infrared carbon monoxide analyzer, and a Horiba Model PIR2000 nondispersive infrared carbon dioxide analyzer. These instruments are calibrated several times per hour using known calibration gases. Instrument outputs are monitored continuously on a Texas Instruments recorder.

Sulfur dioxide is measured using a Dupont Model 411 photometric analyzer. NO_x is measured using the Thermo Electron chemiluminiscent analyzer in conjunction with either a stainless steel or molybdenum converter to convert the NO_2 to NO and thus to obtain a total NO_x reading. A Beckman Model 402 FID hydrocarbon analyzer is used to measure unburned hydrocarbons. The samples for these analyses are transported to the instruments via heated Teflon sample lines and pumped with a heated pump.

Flue gas samples for other unheated lines are withdrawn by a diaphragm-type vacuum pump at two points just upstream of the boiler's draft damper. Each of these sample lines has a porous metal filter at its end to prevent particulate matter from being drawn into the sample line. The lines are periodically back-flushed to prevent blockage of the filter. The sample lines are fed to water-filled bubblers where the sample flow rate from each line is approximately balanced by adjusting the bubbling rates to be approximately equal. The samples are then blended into a single stream which passes through a filter and a Hankison Series E refrigeration-type drier to remove water vapor before being routed to the instruments.

Not all the necessary emission measurements can be made by continuous analyzers. Sample ports are provided in the stack for sampling for particulates, particulate sizing, and trace compounds. Particulates are obtained using EPA Method 5, particulate sizing using an Anderson impactor, and fine particles are measured with an electronic aerosol analyzer.

Stack smoke emissions are normally measured using a Bacharach smoke spot sampler in addition to continuous monitoring of opacity by a Dynatron Model 301 opacity meter; both samples are taken at the boiler exit.

APPENDIX B

SPECIAL SAMPLING METHODS

B-1.1 TRACE ELEMENT, ORGANIC MATERIAL SAMPLING AND ANALYSIS

B-1.1.1 Sample Acquisition

Extensive species measurements were planned for 12 of the 44 coal/RDF suspension combustion tests. These tests include particle sizing trace organics, and trace elements measurement. Obtaining data for these species and pollutant characteristics is most commonly performed using the Source Assessment Sampling System (SASS). However, the availability of an EPA-owned SASS train for use on this project was not realized. The alternate was the use of a modified Aerotherm High Volume Stack Sampler (HVSS). The HVSS train is an EPA Method 5 sampler, which is enlarged to allow 0.08 - 0.11 m^3/min sampling rates. This modified train was used in an EPRI-sponsored program to study the POM emissions from coal-fired utility boilers. The modified HVSS train, in conjunction with a cascade impactor, was used on this program in lieu of a SASS train.

The modified HVSS train is shown in Figure B-1. The major modification to a standard HVSS is the addition of a sample gas conditioner and a glass XAD-2 adsorber unit. The quantity of XAD-2 contained in the adsorber module is similar to that of a SASS train (approximately 7.6 cm diameter x 10.2 cm deep) and has the capacity of 0.11 m^3/min sample rates. In addition, the dual parallel filters allow greater sampling times, in order to minimize the need for filter exchange. Parallel pumps are also used due to the extra pressure drop through the XAD-2 adsorber.

Although the basic sampling system is similar to the SASS, some differences remain. One major change is the loss of the 3 cyclone SASS system (10, 3, and 1μ cut sizes) to a single cyclone of approximately 3-5μ cut size. Since the 3 cyclone SASS system is used in particle size distributions, a cascade impactor was used in conjunction with the modified HVSS train.

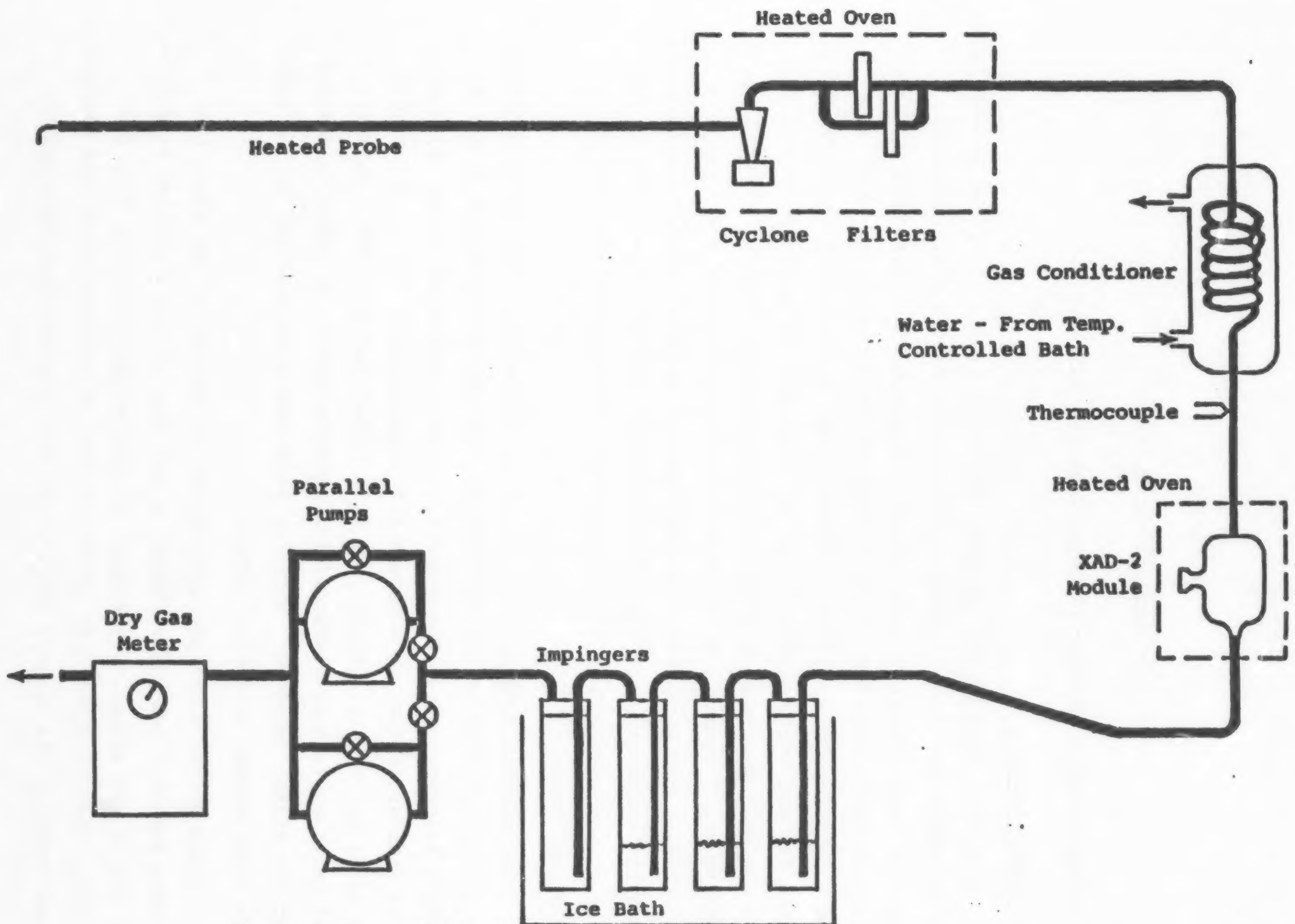

Heated Oven
Heated Probe
Cyclone
Filters
Gas Conditioner
Water - From Temp. Controlled Bath
Thermocouple
Heated Oven
XAD-2 Module
Parallel Pumps
Dry Gas Meter
Impingers
Ice Bath

Figure B-1 . Modified high volume sampling system.

KVB12-26210-1254

Another difference lies in the use and normal operation of the organic module (gas conditioner and XAD-2 module). The SASS train organic module is operated in a condensing mode. The equivalent of the gas conditioner is operated at low enough temperatures to allow water vapor condensation. This flue gas/condensed water flow is allowed to seep through the XAD-2 adsorbent; then some of the water is dropped out and collected. The rest of the water as well as the flue gas then flows to the impinger set. The glass XAD-2 module system shown in Figure B-1 is operated at 328-333°K. The gas conditioner reduces the flow stream temperature to this level; then is allowed to flow through the XAD-2 module which is enclosed in a heated oven. The module is held in a vertical orientation, with the sample flow directed downward, to eliminate a channeling problem.

From the EPRI POM sampling; the end of the sampling train is at the XAD-2 module, and the impinger set was used only to protect the dry gas meter. Therefore, upstream of the XAD-2 module, care was taken to insure that the train was composed of only stainless steel, Teflon or glass and the original lexan impinger bottles were retained. For the combined trace organic, trace element tests, the sampling train includes the impinger set and therefore was constructed of glass, Teflon and stainless. An additional modification which was incorporated was a water dropout collection container, inserted just ahead of the first impinger. This dropout was constructed of stainless steel and glass and is basically an impinger without a submerged inlet tube. Its intent is to increase the system capacity for the water dropout, which has been an operational problem in the past.

In general, the sample train preparation and cleanup followed Level 1 procedures, except where the sampling equipment warranted a change. One major difference was the absence of 2 cyclones and their individual sample collections. This resulted in only a cyclone/probe (>3-5μ) and filter catch (>3-5μ) segregations. These dry particulates were used to determine the particulate loading, as is done for the SASS train. The washes from these particulate sections of the train were collected and stored separately, although this is not specified in Level 1 procedure.

The XAD-2 organic module used for the modified HVSS train also required some changes in the sample cleanup. Since there was no condensate from the organic module, no sample was collected. This module is of glass and Teflon construction and is shipped in modular form. These are not loaded and unloaded for testing, as is done for the SASS organic module, and require a minimum of operator contact.

The impingers were set up as required for Level 1 sampling. The first impinger contained 30 percent H_2O_2 solution to trap reducing gases. The second and third were charged with the $(NH_4)_2S_2O_8$ + A_gNO_3 solution, which is intended to collect the volatile trace elements.

Table B-1 summarizes the types and number of samples collected for the trace elements/organics sampling on the modified HVSS train. The sample cleanup used the same chemicals, containers, and procedures similar to Level 1. The laboratory analyses is similar to Level 1 procedures, but modified for the fewer number of samples and the different adsorber module. This modified sample cleanup is outlined in Figures B-2, B-3, and B-4.

B-1.1.2 Sample Analysis

Table B-2 lists the analyses for the modified HVSS samples, selected gaseous and grab samples. These analyses and techniques are Level 1 measurements, along with some additional tests which focus upon certain species of interest. In addition to these, the gaseous emissions (CO, O_2, etc.) as well as particulate sizing were conducted.

The Level 1 samples are split into three groups for the inorganic, as well as for the bulk of the organic samples. These are the coarse particulate (>3-5μ), fine particulate (<3-5μ) and gaseous. The gaseous section includes the XAD-2 extractions and appropriate impinger solutions. The train washings were combined into each appropriate section for analysis.

The bulk of the trace elements were analyzed with spark source spectrometry (SMSS). In addition, the As, Hg, and Sb elements were measured using atomic absorption, as they are not adequately detected with SSMS.

The organic analysis is based on the Level 1 procedure. This method includes many checks to determine if further analysis is worthwhile, avoiding

TABLE B-1. MODIFIED HVSS TRACE ORGANIC/ELEMENTS SAMPLES

Particulate

1) Cyclone (+ probe/nozzle tappings)

2) Filter

Washes

3) Probe/cyclone (methylene chloride/acetone)

4) Filter (methylene chloride/acetone)

5) Gas conditioner (methylene chloride/acetone)

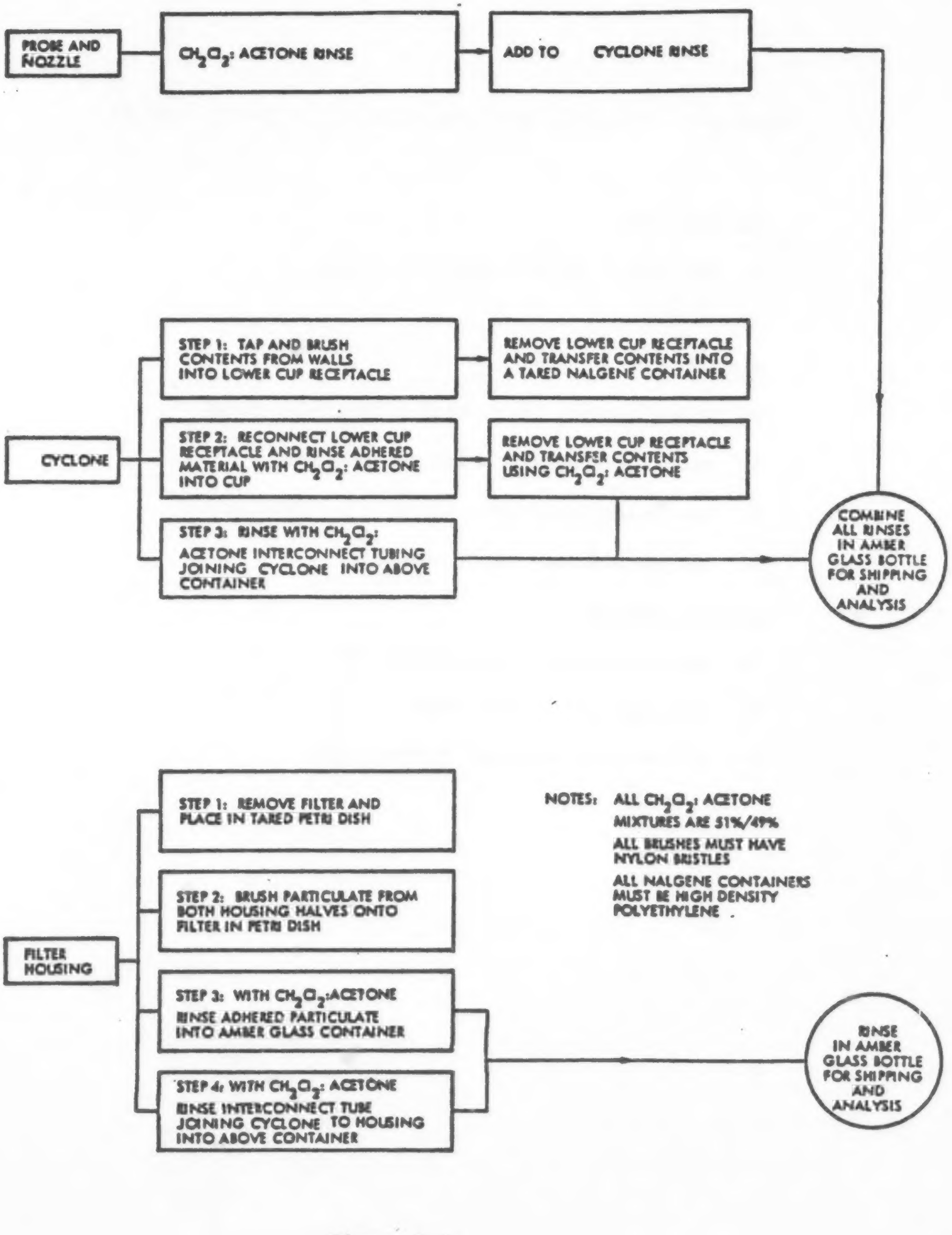
6) Gas conditioner (HNO_3 solution)

Organic Module

7) XAD-2 adsorber (self-contained)

8) 1st impinger + wash (H_2O)

9) 2nd and 3rd impinger + wash (H_2O)


PROBE AND NOZZLE
CH_2Cl_2: ACETONE RINSE
ADD TO CYCLONE RINSE
CYCLONE
STEP 1: TAP AND BRUSH CONTENTS FROM WALLS INTO LOWER CUP RECEPTACLE
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS INTO A TARED NALGENE CONTAINER
STEP 2: RECONNECT LOWER CUP RECEPTACLE AND RINSE ADHERED MATERIAL WITH CH_2Cl_2: ACETONE INTO CUP
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS USING CH_2Cl_2: ACETONE
STEP 3: RINSE WITH CH_2Cl_2: ACETONE INTERCONNECT TUBING JOINING CYCLONE INTO ABOVE CONTAINER
COMBINE ALL RINSES IN AMBER GLASS BOTTLE FOR SHIPPING AND ANALYSIS
FILTER HOUSING
STEP 1: REMOVE FILTER AND PLACE IN TARED PETRI DISH
STEP 2: BRUSH PARTICULATE FROM BOTH HOUSING HALVES ONTO FILTER IN PETRI DISH
STEP 3: WITH CH_2Cl_2:ACETONE RINSE ADHERED PARTICULATE INTO AMBER GLASS CONTAINER
STEP 4: WITH CH_2Cl_2: ACETONE RINSE INTERCONNECT TUBE JOINING CYCLONE TO HOUSING INTO ABOVE CONTAINER
RINSE IN AMBER GLASS BOTTLE FOR SHIPPING AND ANALYSIS

NOTES: ALL CH_2Cl_2: ACETONE MIXTURES ARE 51%/49%

ALL BRUSHES MUST HAVE NYLON BRISTLES

ALL NALGENE CONTAINERS MUST BE HIGH DENSITY POLYETHYLENE.

Figure B-2.

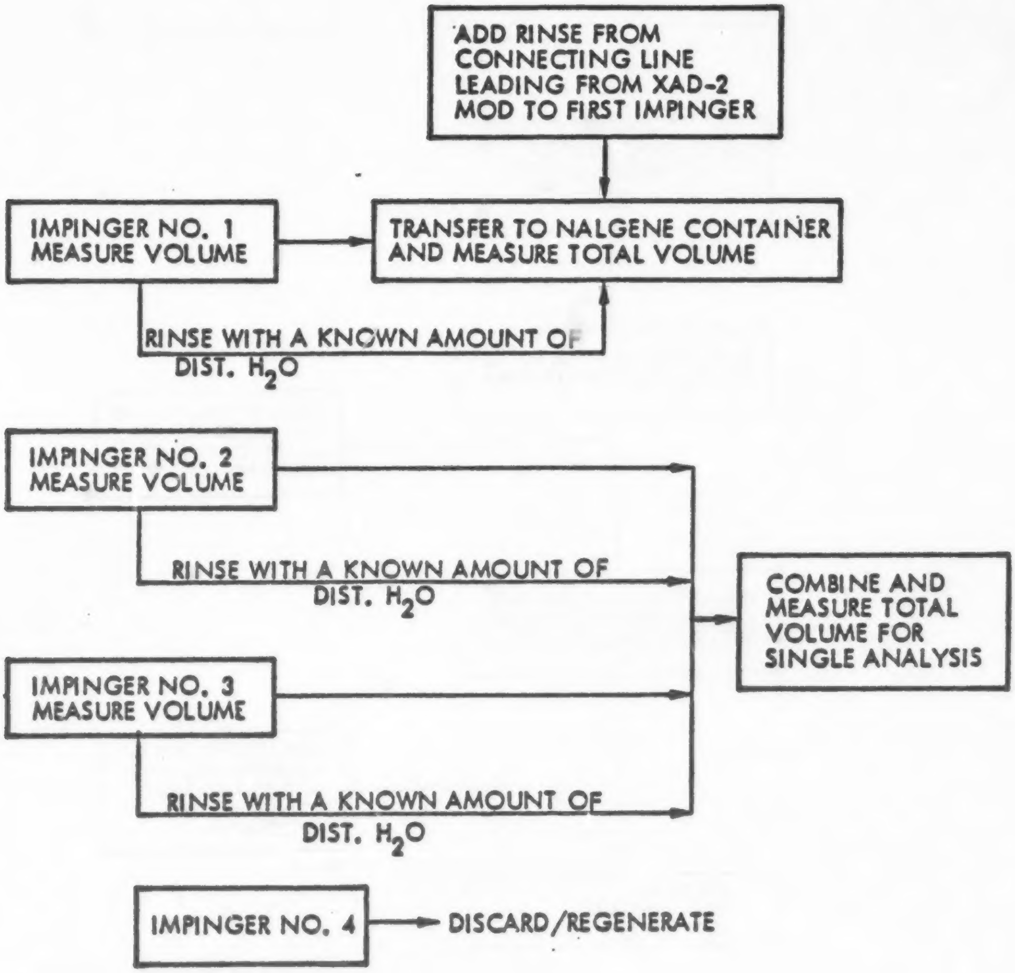
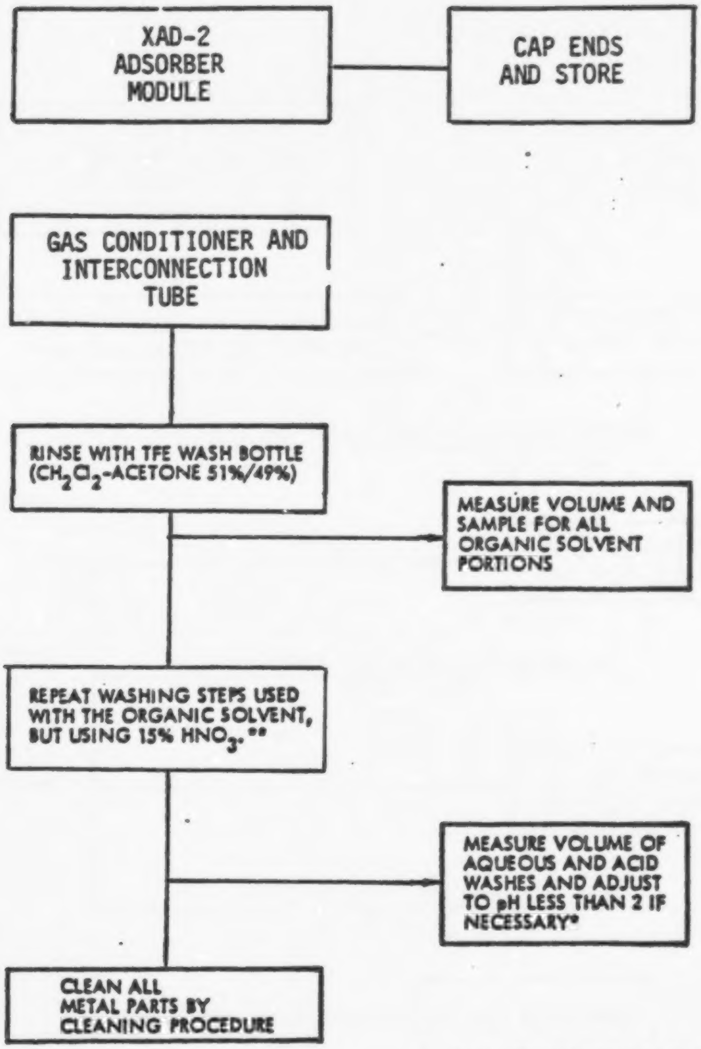

ADD RINSE FROM CONNECTING LINE LEADING FROM XAD-2 MOD TO FIRST IMPINGER
IMPINGER NO. 1 MEASURE VOLUME
TRANSFER TO NALGENE CONTAINER AND MEASURE TOTAL VOLUME
RINSE WITH A KNOWN AMOUNT OF DIST. H2O
IMPINGER NO. 2 MEASURE VOLUME
RINSE WITH A KNOWN AMOUNT OF DIST. H2O
COMBINE AND MEASURE TOTAL VOLUME FOR SINGLE ANALYSIS
IMPINGER NO. 3 MEASURE VOLUME
RINSE WITH A KNOWN AMOUNT OF DIST. H2O
IMPINGER NO. 4
DISCARD/REGENERATE

Figure B-3.


XAD-2 ADSORBER MODULE
CAP ENDS AND STORE
GAS CONDITIONER AND INTERCONNECTION TUBE
RINSE WITH TFE WASH BOTTLE (CH_2Cl_2-ACETONE 51%/49%)
MEASURE VOLUME AND SAMPLE FOR ALL ORGANIC SOLVENT PORTIONS
REPEAT WASHING STEPS USED WITH THE ORGANIC SOLVENT, BUT USING 15% HNO_3.**
MEASURE VOLUME OF AQUEOUS AND ACID WASHES AND ADJUST TO pH LESS THAN 2 IF NECESSARY*
CLEAN ALL METAL PARTS BY CLEANING PROCEDURE

* CAN USE pH PAPER FOR THIS STEP

** "15%" HNO_3 IS MADE BY COMBINING ONE VOLUME 70% HNO_3 AND FOUR VOLUMES H_2O.

Figure B-4.

TABLE B-2. TRACE ELEMENT/ORGANICS ANALYSIS

		Source			Coarse	Fine	
Species	Method	Gaseous	Coal	RDF	Part.	Part.	Gaseous
Inorganic							
HCl (MI)	SI	12					
HF (MI)	SI	12					
HBr (MI)	SI	12					
Li-U Elements	SSMS		1	1	12	12	12
As	AAS		1	1	12	12	12
Hg	AAS		1	1	12	12	12
Sb	AAS		1	1	12	12	12
Organic							
Mass C_8-C_{12}, T CO	GC/FID				12	12	12
Mass gravimetric	Weigh				12	12	
Organic Classes	FTIR				12	12	12
LC Fractions*	Silica gel				12	12	12
Fraction Mass, T CO*	GC/FID				12	12	12
Fraction Mass, Grav*	Weigh				12	12	12
Classes in Fractions*	FTIR				12	12	12
Compounds in Fract's*	LRMS				12	12	12
Organic Chlorine	AAS				12	12	12
POM Species	GC/MS				--	4	--
PCB Class Id.†	GC/EC				--	12	--
Dioxin Species†	GC/MS				--	3	--
PCB Species§	GC/MS				--	3	--

* Level 1 criteria.

† Conducted if organic chlorine >58 μg/m^3 or 0.003 μg/g in solids.

§ Conducted if PCB class concentration >500 μg/m^3 or 0.002 μg/g in solids.

unnecessary costs. This is particularly important since the most comprehensive tests are the most costly, but require an adequate sample for a valid analysis. In addition, tests were included to determine organic chlorine and PCB's. These chlorine compounds are important because of the chlorine content of the RDF. As shown, all tests up to and including the organic chlorine analysis were performed on each sample run.

The last four analyses listed are the extensive POM and PCB tests. Since these are the most costly tests, the samples used here were a composite of the coarse/fine particulates and the gaseous sections of the train. In this manner, the result of these analyses were a total, rather than an unknown fraction of the collected sample (if only one of the three samples were chosen). The POM species analysis was planned for one coal and one of each of these coal/RDF tests. The PCB and dioxin tests are based on a criteria system to avoid unnecessary tests. These cutoff points are those suggested by Battelle and are based on MATES values.

B-1.2 GOKSOYR-ROSS TECHNIQUE FOR SO_3 DETERMINATION

The SO_3 concentrations in the flue gas were determined using Goksoyr-Ross Technique. A schematic of the apparatus is shown in Figure B-5. This

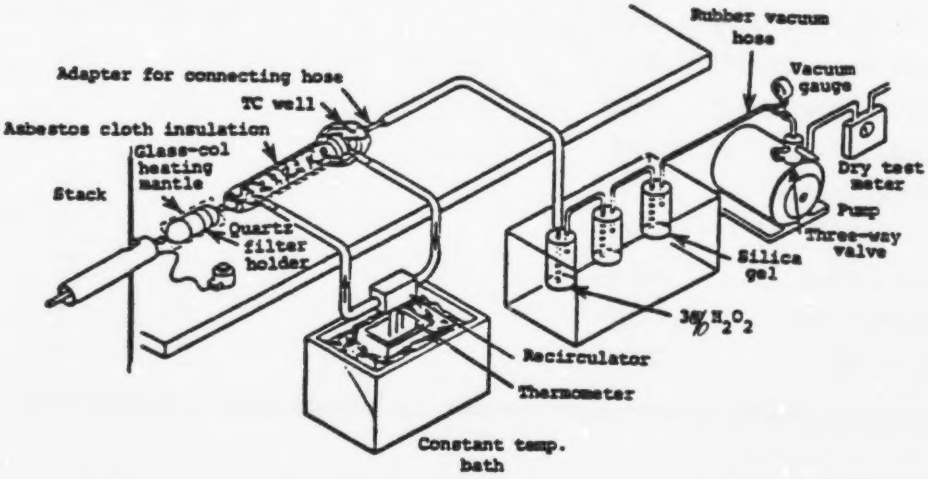

Rubber vacuum hose
Adapter for connecting hose
Vacuum gauge
TC well
Asbestos cloth insulation
Glass-col heating mantle
Dry test meter
Stack
Pump
Quartz filter holder
Three-way valve
Silica gel
3% H_2O_2
Recirculator
Thermometer
Constant temp. bath

Figure B-5. Schematic of the Goksoyr-Ross approach.

apparatus, developed by Goksoyr and Ross, is essentially a liquid-cooled condenser which allows a controlled condensation of H_2SO_4 while preventing water condensation.

TEST PROCEDURE

1. Wash the coil and probe with 5% IPA and rinse with acetone to dry each piece. Assemble the coil and probe and insert a plug of quartz wool in the probe inlet. The coil outlet is connected to an impinger (filled with approximately 100 ml water) and to a dry gas meter and pump.
2. The coil water jacket temperature should be maintained between 333°K and 339°K. The probe should be maintained above 367°K.
3. The system should be leak checked and be virtually free of any leakage. This is because the sample volume is low and the system vacuum is usually quite high (caused largely by the frit in the coil).
4. Begin drawing a sample through the system at the rate of 2.1×10^{-3} m^3/min. This will produce .042 m^3 in 20 minutes which has been adequate for most conditions.
5. On completion of sampling, remove the probe and coil. While the probe is cooling, wash the coil with approximately 10 ml of 5% IPA into a clean flask. Repeat this wash three times so that the coil has been washed twice in each direction. Rinse the coil with acetone and set it aside. Remove the quartz plug from the probe (save if necessary) and wash the probe into the above flask with 10 ml of 5% IPA. This should leave approximately 50 ml of IPA for titration. Rinse with acetone and prepare for the next test.
6. During the sampling, the following items should be recorded:
   a. Starting time
   b. Starting volume
   c. Coil temperature
   d. Probe temperature
   e. Duct temperature

   f. O_2
   g. Finish time
   h. Finish volume
7. Titrating sample wash
   a. Use the entire IPA wash
   b. Add 3-5 drops bromophenol blue indicator
   c. Titrate with NaOH (Step 1, chemistry)

      The end point is reached when the indicator goes from yellow to blue
   d. Record the amount of titrant used
   e. Calculate SO_3 concentration:

$$SO_3, \text{ ppm} = \frac{416 \times N \times A}{V}$$

where: N - normality of NaOH
A - ml of NaOH
V - corrected sample volume

CHLORIDE, FLUORIDE AND BROMIDE SAMPLING TRAIN AND SAMPLING PROCEDURES

Sample Train

Figure B-6 shows a schematic of the halogen sampling system. It consisted of a heated probe and filter, an impinger train, ice bath, dry gas meter, and a pump.

A 0.28 m^3 sample was collected at a 0.014 m^3/min rate from the stack, during which time all stainless steel parts of the train were maintained above 422°K. In order to prevent reactions between hydrogen fluoride and the plastics in the system when exposed to light, the impinger train was covered with aluminum foil.

Following the sample collection, the front end and the lines between impingers were washed with distilled water and added to the sample.

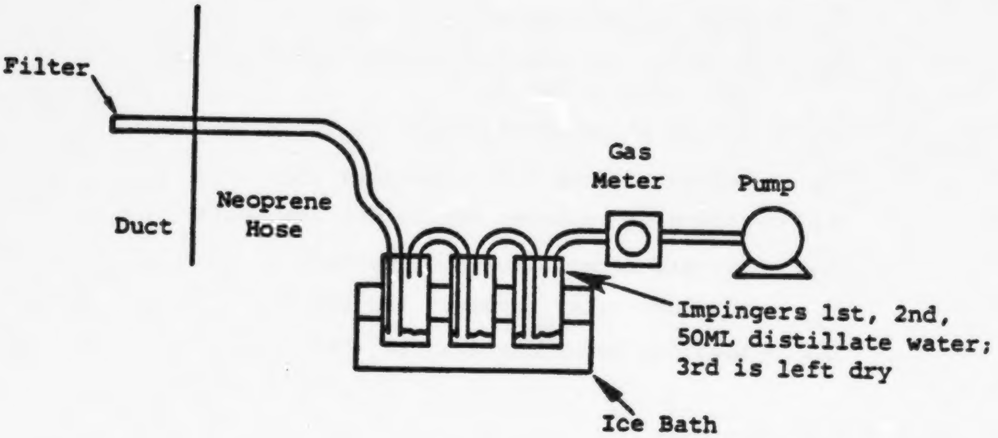

Filter
Duct
Neoprene Hose
Gas Meter
Pump
Impingers 1st, 2nd, 50ML distillate water; 3rd is left dry
Ice Bath

Figure B-6. Schematic of the halogen sampling system.

Sample Analysis

Orion specific ion electrodes were used to measure the ion concentrations of the chloride, fluoride, and bromide directly.

The procedures used in the analysis were basically as described in the Orion Specific Ion Electrode manuals for each halogen.

The sample as obtained from the train was split into the proportions required to conduct the analysis of each halogen. In some instances dilution of the sample was necessary to maintain satisfactory ion concentrations.

The analysis required preparation of a calibration curve for each halogen from which ionic strength could be related to molar concentrations of the species in the sample solution.

The concentration of the specie was then calculated using the following equation:

$$C_s \text{ (ppm dry)} = 0.2553 \frac{C_{si} \times V_{si} \times V_T \times T_{gm}}{V_s \times V_{gm} \times P_{gm}}$$

where

C_s = stack concentration - dry (ppm)

C_{si} = specific ion electrode molar concentration (for calibration curve)

V_{si} = volume of detected sample (ml)

V_s = volume of sample for analysis (ml)

V_T = volume of impinger sample and wash (ml)

V_{gm} = dry gas meter sample volume (m^3)

P_{gm} = absolute meter pressure (in Pa)

T_{gm} = absolute meter temperature (°K)

Particle Sizing Procedure

Particle size distributions were obtained using a Metrology Research Instruments (MRI) cascade type impactor. The particular impactor can be assembled with a variety of particle size stages. All experiments in this program were conducted using seven stages ranging from 0.4 micron to 1.6 micron size in addition to a final stage containing a disk filter. A schematic of the impactor is given in Figure B-7.

Sampling was accomplished by drawing flue gas through the impactor and a gas meter by means of a sample pump. The flow rate was approximately 0.020 cubic meters per minute to achieve isokinetic flow through the inlet nozzle. Normally a five- to ten-minute sample time would yield an optimum sample mass on each impactor stage.

Mass determination at each stage was made by stage plate weight changes (with and without sample) using an analytical balance.

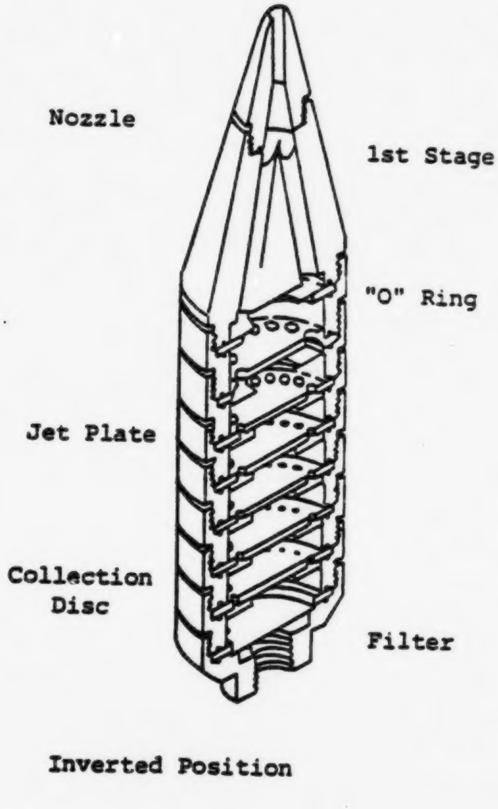

Nozzle
1st Stage
"O" Ring
Jet Plate
Collection Disc
Filter
Inverted Position

Figure B-7. Assembly drawing of model of Model 1502 inertia cascade impactor.

APPENDIX C

BATTELLE REPORT

FINAL REPORT

on

ANALYSIS OF ORGANIC AND INORGANIC POLLUTANT SAMPLES FROM INDUSTRIAL BOILER EMISSIONS

to

KVB, INC.

April 28, 1981

by

Rachael Barbour

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

ACKNOWLEDGEMENT

We gratefully acknowledge the advice and assistance of Mr. John Arand of KVB, Inc.

SECTION I

INTRODUCTION

The exhaust of an industrial boiler, co-firing refuse derived fuel and coal, was sampled by KVB, Inc., using a high volume sampling system (HVSS) train. Particulate matter, filters, gases collected on a sorbent column, impinger solutions and train rinses were collected and submitted to Battelle for Level 1 organic and inorganic analyses. These procedures were carried out according to the procedures cited in the following reference:

> IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition), EPA-600, 7-78-201, October, 1978.

Several additional analyses were requested including analysis for organic chlorines, dioxins, polynuclear aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs).

Because of time and budget limitations, the test runs were prioritized by KVB, Inc. The highest priority group of samples was A, D, E, O, S, and 1 and the second priority group was B, M, R, 2, and 3. Samples C and N were of little interest and no further work was done after the date that these priorities were set (September 19, 1980). This approach resulted in no analysis of sample N, hence no results are presented for this sample.

SECTION 2
EXPERIMENTAL

LEVEL 1 ANALYSIS

Samples were received and analyzed as shown in Table 1. Analysis methods included spark source mass spectrometry (SSMS), atomic absorption spectrophotometry (AAS), total chromatographable organics (TCO), gravimetric organics (GRAV), infrared spectroscopy (IR) and low resolution mass spectrometry (LRMS).

Organic Analysis

Samples for organic analysis were extracted with methylene chloride. These extractions were used for determination of volatiles by gas chromatography, nonvolatiles by gravimetric analysis, and infrared analysis. Samples collected in the oven portion of the samples (cyclone catches and particulate filter) did not require analysis of the volatiles since the oven temperature was sufficient to volatilize any species present. Those samples for which the total organic loading (volatiles plus nonvolatiles) exceeded 15 mg were fractionated by liquid chromatography (LC). The liquid chromatography included 7 fractions from non-polar (pentane) to polar (50:50 mixture of methylene chloride and methanol). All LC fractions were analyzed by gravimetry, gas chromatography and infrared spectroscopy.

Inorganic Analysis

Cyclone catches, particulate filters, XAD-2, and impinger solutions were analyzed for elements Li-U by spark source mass spectrometry (SSMS). These same samples were also analyzed for Mercury (Hg) by atomic absorption spectrophotometry (AAS). In addition, combined 2nd and 3rd impinger solutions were analyzed by AAS for antimony and arsenic (Sb and As).

SPECIAL ANALYSES

Analyses requested which were not required under Level 1 guidelines included organic chlorines, dioxins, polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs).

PAH Analysis

The organic extracts of the particulate filters were first screened for PAHs by a fluorescence spot test. This spot test is explained more fully in the following reference:

> E. M. Smith and P. L. Levins, "Sensitized Fluorescence for the Detection of Polycyclic Aromatic Hydrocarbons", EPA-600/70780182, September, 1978.

The technique is based on the sensitization of the inherent fluorescence of PAHs and can routinely detect compounds present at the 10 pg level. Accuracy is reported within one order of magnitude.

Only two samples were positive for PAH using this spot test: filter extracts from runs 1 and 3 at a level of 10^{-3} g/l. It was decided to run the filter extracts from runs 0 and S as well, even though the spot test did not show any PAH present. This decision was based on the fact that doing 4 PAH analyses was not much more work than two due to extensive calibrations needed.

These four samples were quantitatively analyzed for PAHs by electron impact gas chromatography/mass spectrometry (GC/MS) using a 30 m SE-52 capillary column. The column was temperature programmed from 100-320°C at 3° C/min., holding at the upper temperature until completion of the analysis. The injector, transfer line, and separator oven temperatures were 300° C.

The specific method involved full mass scans from 100 - 350 dalton. Quantification was achieved by plotting the mass chromatogram of the molecular ion and integrating the arc beneath the curve.

PCB and Dioxin Analyses

Organic extracts were analyzed for total organic chlorine content. The samples were screened for PCBs using GC with a Hall electrolytic conductivity detector. The chromatographic conditions used were as follows:

GC - Tracer 710A

Column - 6 ft. X 2 mm I.D. glass packed with 3% SP-2250 on Supelcoport 100/120 Mesh

Temperature Program - 60-240° C at 8° C/min.

Injector Volume - 2 μl

Solvent - Cyclopentane

Quantification was conducted by comparing peak areas of the sample components to the area of an external standard (tetrachlorobiphenyl).

The original criterion for PCB and dioxin analysis was that any extract of the particulate which exceeded 58 $\mu g/m^3$ at the source would be analyzed for dioxins and PCB compounds. No partciulate filter extracts exceeded this number. There was a further criterion stating that any of these samples exceeding 500 $\mu g/m^3$ of PCBs would be analyzed for PCB species. No sample approached this level of PCB concentration.

Because the XAD-2 extracts consistently showed organic chlorines, these were analyzed by glass capillary gas chromatography/high resolution mass spectrometry (HRGC/HRMS) for TCDD, by far the most toxic of the dioxins. First the sample is cleaned by liquid chromatography on an alumina column and spiked with 6 ng of a ^{13}C labeled internal standard. Although the absolute detection limit of this method is 0.7 pg, the actual detection limit is a function of the noise level due to the sample matrix. In this case, the effective detection limit was increased because only 1% of the sample was used in the analysis. Nonetheless, the detection limit for these samples, calculated back to the source is approximately 0.1 part per trillion which is well below toxicity levels for TCDD.

FUEL ANALYSIS

Samples of two fuels used in the industrial boiler were also received for analysis. These were coal and refuse derived fuel. Both were subjected to AAS analysis for mercury, arsenic, and antimony. Both also were analyzed for elements Li-U by SSMS.

SECTION 3
RESULTS

ORGANICS

For the unfractionated samples, organic material was distributed in the normal manner. That is, the majority of organic material was found in the XAD-2 and in the combined washes. Organics in the filter and cyclone catches were less by a factor of between 10 and 100. Somewhat surprising was that the sample having by far the most organic material was the combined washes from run A (coal only). Had the XAD-2 from this run been highly loaded it would appear that the sorbent had been overloaded causing the washes to have a high organic content. On the contrary, the XAD-2 from run E (50% CEA RDF, 50% coal) had the most organics of any XAD-2 by a factor of 10. Thus the origin of high organic loading in the run A washes in unclear. Organic loadings for both unfractionated and fractionated samples are given in Tables 2-16.

The distribution of organics in the fractionated material indicated that for the majority of samples most of the organic material was in Fraction 6, a highly polar fraction. This means that oxidized species such as ketones, amines and phenols account for a large part of these samples. Two samples varied from this trend: the XAD-2 extracts for runs 1 and E. Run 1, which burned 9.4% waste oil/40% CEA RDF/50% coal had 75% of the organics from XAD-2 in Fraction 3. From a health standpoint this would be of great interest as Fraction 3 can contain polynuclear aromatics (PNAs) and polychlorinated biphenyls (PCBs). The XAD-2 from run E (50% CEA RDF/50% coal) had organic material distributed as follows: 25% in Fraction 2, 32% in Fraction 3, and 27% in Fraction 6. This raises the same point as run 1; that is, there is a significant amount of material in fractions which tend to contain PCBs and PNAs.

Infrared spectra obtained on each unfractionated organic sample gave information concerning the composition of these samples. These data are shown in Table 17. Many components were those expected from any combustion source: carboxylic acids, other carbonyl containing compounds, aliphatic hydrocarbons and anhydride. In addition, several of the combined washes contained inorganic nitrate. Two compounds seen were suspected to be contaminants: silicone (a common lubricant) and tri cresyl phosphate (a plasticizer). Several unusual species were found however, especially in the infrared spectra of the fractions with further information from low resolution mass spectrometry (LRMS). Infrared results for fractionated samples are given in Tables 18-30 and LRMS in Table 31. Doubly conjugated ketones were found in runs A, M, and S; aromatic amides and/or amines in runs A, D, E, M, S, and 1; isocyanate in runs A, E, and M, and organic nitro compounds in run C only. Also urethane was found in runs C, D, and E. Since urethane is certainly not a normal combustion product and since it only appears when CEA RDF was burned, it could be that urethane was in the refuse used to derive the fuel. Another unusual compound was triazine, isolated in run 1.

INORGANICS

SSMS results are given in Appendix 1. About half the samples run showed low levels of lead. Results of analysis for mercury, antimony and arsenic by atomic absorption (AAS) are given in Tables 32-37. XAD-2 samples had more mercury than other types of samples (filters, particulates, impinger solutions). The XAD-2 from run E had the most mercury of the XAD-2s by a factor of 10. Antimony was not detected in any sample. Arsenic was very low or not detected.

PAH ANALYSIS

As expected from the results of the spot test, levels of PAH were low in these samples. Runs 1 and 3, which were the two showing PAH by the spot test, had the most PAH. The two PAHs with the highest concentrations were benzofluoranthene and coronene. Results are given in Table 38.

PCB AND DIOXIN ANALYSIS

Before PCB and dioxin analysis, organic chlorine content was determined. These results are given in Tables 40-43. The combined washes and XAD-2 extracts had low levels of organic chlorine while the filters and particulates had none. Examination of the gas chromatograms did show that 12 samples probably contained trace levels of tetrachlorobiphenyl. These are listed in Table 45.

The results of the dioxin analysis were all negative. That is, no TCDD was seen above detection limits which in this case translated to 0.1 part per trillion at the source. Results are given in Table 44.

FUEL ANALYSIS

Neither the coal nor the refuse derived fuel showed any antimony. Coal had four times the arsenic of the RDF and the RDF had six times the mercury in coal. AAS results are given in Table 46, SSMS results in the Appendix.

TABLE 1. LIST OF SAMPLES RECEIVED AND A BREAKDOWN OF ANALYSES PERFORMED

	Extraction	GRAV TCO* IR	SSMS	AAS (Hg)	AAS (Sb, As)	LC-IR-LRMS**
XAD-2 Sorbent Cartridge						
A 79	X	X	X	X		X
B 81	X	X	X	X		
C 80	X	X	X	X		X
D 72	X	X	X	X		X
E 329	X	X	X	X		X
M-9	X	X				X
O-9	X	X				X
R-9	X	X				
S-9	X	X				X
1-9	X	X				X
2-9	X	X				
3-9	X	X				
Particulate Filters						
A 6	X	X	X	X		
B 8	X	X	X	X		
C 7	X	X	X	X		
D 7	X	X	X	X		
E 7	X	X	X	X		
M-7	X	X	X	X		
O-7	X	X	X	X		
R-7	X	X	X	X		
S-7	X	X	X	X		
1-7	X	X	X	X		
2-7	X	X	X	X		
3-7	X	X	X	X		
Cyclone Catch						
B 7	X	X	X	X		
C 8	X	X	X	X		
D 8	X	X	X	X		
E 8	X	X	X	X		
M-8	X	X	X	X		
O-8	X	X	X	X		
R-8	X	X	X	X		
S-8	X	X	X	X		
1-8	X	X	X	X		
2-8	X	X	X	X		
3-8	X	X	X	X		

---

* Some samples were collected in the oven and due to the temperature, no volatiles are present.

** Only performed if minimum of 15 mg sample available.

TABLE 1. (CONTINUED)

	Extraction	GRAV TCO* IR	SSMS	AAS (Hg)	AAS (Sb, As)	LC-IR-LRMS**
Organic Washes (Combined)						
A1/A4/A5	X	X	X	X		X
B3/B4/B5/B6	X	X	X	X		
C3/C4/C5/C6	X	X	X	X		X
D3/D4/D5/D6	X	X	X	X		X
E3/E4/E5/E6	X	X	X	X		X
M3/M4/M5/M6	X	X				
O3/O4/O5/O6	X	X				
R3/R4/R5/R6	X	X				
S3/S4/S4/S6	X	X				
1-3/1-5/1-6		X				
2-3/2-5/2-6		X				
3-3/3-5/3-6		X				
First Imginger Solution						
A 3			X	X		
B 1			X	X		
C 1			X	X		
D 1			X	X		
E 1			X	X		
M-1			X	X		
O-1			X	X		
R-1			X	X		
S-1			X	X		
1-1			X	X		
2-1			X	X		
3-1			X	X		
Second and Third Impinger Solution						
A 2				X	X	
B 2				X	X	
C 2				X	X	
D 2				X	X	
E 2				X	X	
M 2				X	X	
O 2				X	X	
R 2				X	X	
S 2				X	X	
1-2				X	X	
2-2				X	X	
3-2				X	X	

---

* Some samples were collected in the oven and due to the temperature, no volatiles are present.

** Only performed if minimum of 15 mg sample available.

TABLE 2. ORGANIC COMPOSITION DETERMINED GRAVIMETRICALLY ON COMBINED WASHES

Sample I.D.	Nonvolatiles* (mg/sample)
A1/A4/A5	1400
B3/B4/B5/B6	6.1
C3/C4/C5/C6	17
D3/D4/D5/D6	21
E3/E4/E5/E6	13

* Due to oven temperature at sample collection, no volatiles are present.

TABLE 3. ORGANIC COMPOSITION DETERMINED GRAVIMETRICALLY ON PARTICULATE FILTERS AND CYCLONE CATCHES

Filters	Nonvolatiles* (mg/sample)
A6	1.4
B8	0.6
C7	0.7
D7	1.0
E7	0.9
M-7	0.2
O-7	0.4
R-7	0.4
S-7	0.5
1-7	0.6
2-7	0.2
3-7	0.4
Cyclone Catch	
B7	1.7
C8	1.5
D8	1.1
E8	1.2
M-8	0.9
O-8	0.1

* Due to oven temperature at sample collection, no volatiles are present.

TABLE 3. (CONTINUED)

Cyclone Catch	Nonvolatiles* (mg/sample)
R-8	0.3
S-8	0.2
1-8	0.4
2-8	0.1
3-8	0.2

* Due to oven temperature at sample collection, no volatiles are present.

TABLE 4. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON XAD-2 SORBENT CARTRIDGES

Sample I.D.	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
A79	5.7	24	29.7
B81	3.6	12	15.6
C80	5.3	18	23.3
D72	21	25	46
E329	94	28	122
M-9	10	25	35
0-9	12	29	41
R-9	7.0	18	25
S-9	10	29	39
1-9	19	42	61
2-9	6.0	13	19
3-9	5.0	14	19

TABLE 5. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTIONS OF COMBINED WASHES, RUN A

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	0.1	1.8	1.9
2	ND	1.2	1.2
3	24	100	124
4	0.6	450	450.6
5	170	130	300
6	55	720	775
7	4.6	5.8	10.4

ND = not detected.

TABLE 6. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTIONS OF XAD-2, RUN A

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	ND	0.8	0.8
2	ND	0.8	0.8
3	ND	0.9	0.9
4	ND	1.5	1.5
5	ND	1.1	1.1
6	5.2	17	22.2
7	0.3	1.8	2.1

TABLE 7. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTIONS OF COMBINED WASHES, RUN C

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	4.1	2.0	6.1
2	ND	0.6	0.6
3	0.5	0.9	1.4
4	ND	1.5	1.5
5	ND	1.6	1.6
6	8.7	7.4	16.1
7	1.7	3.0	4.7

TABLE 8. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTION OF XAD-2, RUN C

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	ND	0.5	0.5
2	ND	0.4	0.4
3	ND	0.5	0.5
4	0.4	0.5	0.9
5	ND	0.8	0.8
6	4.1	15	19.1
7	0.8	0.6	1.4

TABLE 9. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTIONS OF COMBINED WASHES, RUN D

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	0.1	4.3	4.4
2	ND	ND	ND
3	0.3	0.2	0.5
4	0.3	0.2	0.5
5	ND	0.2	0.2
6	0.7	12	12.7
7	0.3	4.4	4.7

TABLE 10. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTIONS OF XAD-2, RUN D

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	1.3	0.2	1.5
2	1.8	0.1	1.9
3	2.4	0.9	3.3
4	ND	0.2	0.2
5	4.7	1.3	6.0
6	7.5	22	29.5
7	3.2	0.7	3.9

TABLE 11. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTIONS OF COMBINED WASHES, RUN E

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	1.6	1.8	3.4
2	ND	ND	ND
3	0.4	ND	0.4
4	2.5	2.5	5.0
5	2.6	ND	2.6
6	12	4.3	16.3
7	ND	3.8	3.8

TABLE 12. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTIONS OF XAD-2, RUN E

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	5.3	1.1	6.4
2	30	0.3	30.3
3	34	4.4	38.4
4	ND	2.8	2.8
5	0.2	2.8	3.0
6	16	17	33
7	7.6	0.4	8.0

TABLE 13. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTIONS OF XAD-2, RUN M

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	0.1	1.0	1.1
2	ND	ND	ND
3	0.1	0.1	0.2
4	0.9	1.0	1.9
5	1.7	1.1	2.8
6	5.7	21	27
7	1.6	0.3	1.9

TABLE 14. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTIONS OF XAD-2, RUN 0

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	0.4	0.4	0.8
2	ND	ND	ND
3	0.1	ND	0.1
4	0.8	1.1	1.9
5	2.3	1.4	3.7
6	6.9	26	36
7	1.7	0.3	2.0

TABLE 15. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES ON LIQUID CHROMATOGRAPHY FRACTIONS OF XAD-2, RUN S

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	0.3	1.7	2.0
2	0.2	ND	0.2
3	0.2	0.3	0.5
4	0.9	1.1	2.0
5	2.3	1.5	3.8
6	4.6	24	29
7	1.5	0.2	1.7

TABLE 16. ORGANIC COMPOSITION DETERMINED BY GRAVIMETRIC AND GAS CHROMATOGRAPHIC ANALYSES OF LIQUID CHROMATOGRAPHY FRACTIONS OF XAD-2, RUN 1

Fraction Number	Volatiles (mg/sample)	Nonvolatiles (mg/sample)	Total (mg/sample)
1	1.1	0.7	1.8
2	0.3	0.3	0.6
3	5.1	40	45
4	4.1	1.5	5.6
5	3.0	ND	3.0
6	3.9	ND	3.9
7	1.6	ND	1.6

TABLE 17. INFRARED RESULTS FOR TOTAL ORGANIC EXTRACTS

Sample	Interpretation
Run A	
Combined Washes	Predominantly short chain acid, some amine and other carbonyl containing compounds.
XAD-2	Benzoic acid, some hydrocarbon and small amounts of anhydride.
Run B	
Combined Washes	Large amount of inorganic nitrate. Small amounts of carboxylic acid salt and aliphatic hydrocarbon.
Cyclone Catch	Aliphatic hydrocarbon with ester and acid. Very little material present.
Particulate Filter Catch	Aliphatic ester and ether with a small amount of tricresyl phosphate.
XAD-2	Inorganic Si-O compound, several carbonyl containing compounds and aliphatic hydrocarbon.
Run C	
Combined Washes	Carbonyl containing compound which is possibly urethane, an organic nitro compound and inorganic nitrate.
Particulate Filter Catch	Predominantly tricresyl phosphate with aliphatic ester and aliphatic ether.
Cyclone Catch	Aliphatic hydrocarbon and ester plus organic Si-O.
XAD-2	Predominantly aromatic ester with aliphatic hydrocarbon and some carboxylic acid.

TABLE 17. (CONTINUED)

Sample	Interpretation
Run D	
Combined Washes	Large amount of inorganic nitrate and small amounts of urethane, carboxylic acid salt, aliphatic hydrocarbon and silicone.
Particulate Filter Catch	Predominantly aliphatic ester, some aliphatic ether and aromaticity. Very small amount of tri cresyl phosphate.
Cyclone Catch	Aliphatic hydrocarbon, ester and some carboxylic acid. Very little material present.
XAD-2	Benzoic acid, aliphatic hydrocarbon, small amount of ester and trace of carbocylic acid salt.
Run E	
Combined Washes	Large amounts of inorganic nitrate and small amounts of urethane, carboxylic acid salt and aliphatic hydrocarbon.
Particulate Filter Catch	Aliphatic ester and ether with a small amount of tricresyl phosphate.
Cyclone Catch	Inorganic Si-O with aliphatic hydrocarbon and ester. Very little material present.
XAD-2	Benzoic acid, benzoic acid ester and aliphatic hydrocarbon.
Run M	
Combined Washes	Doubly conjugated ketone and carboxylic acid. Evidence for aromatic amide. Isocyanate is present.
Particulate Filter Catch	Aliphatic hydrocarbon with small amounts of two carbonyl containing compounds, one of which is probably ester. Some aromaticity.

TABLE 17. (CONTINUED)

Sample	Interpretation
Run M	
Cyclone Catch	Same as particulate filter except less ester and less aromaticity.
XAD-2	Predominantly benzoic acid.
Run O	
Combined Washes	Inorganic nitrate.
Particulate Filter Catch	Aliphatic hydrocarbon with a small amount of aromatic ester. Trace amounts of two other carbonyl containing compounds.
Cyclone Catch	Aliphatic hydrocarbon with small amounts of several carbonyl containing compounds.
XAD-2	Predominantly benzoic acid.
Run R	
Particulate Filter Catch	Branched hydrocarbon with small amounts of two carbonyl containing compounds.
Cyclone Catch	Aliphatic hydrocarbon with trace amounts of carbonyl containing compounds.
XAD-2	Predominantly benzoic acid.
Run S	
Combined Washes	Doubly conjugated ketone.
Particulate Filter Catch	Aliphatic hydrocarbon with a small amount of aliphatic ester. There is some aromaticity and a trace amount of tricresyl phosphate.
Cyclone Catch	Aliphatic hydrocarbon with branched end groups. Trace amounts of anhydride and another carbonyl, probably ester.

TABLE 17. (CONTINUED)

Sample		Interpretation
Run S	XAD-2	Aliphatic ester and benzoic acid.
Run 1	Combined Washes	Branched hydrocarbon and small amount of ester.
	Particulate Filter Catch	Short chain acid, amine and a high frequency carbonyl which may be anhydride. There is significant aromaticity.
	Cyclone Catch	Anhydride ester and carboxylic acid (short chain), all in low concentration.
	XAD-2	Benzoic acid, other short chain acid and aromatic ester.
Run 2	Particulate Filter Catch	Aliphatic hydrocarbon with very small amounts of two carbonyl containing compounds.
	Cyclone Catch	Aliphatic hydrocarbon with small amounts of two carbonyl containing compounds, only one of which is the same as on the particulate filter.
	XAD-2	Benzoic acid, short chain carboxylic acid and a third carbonyl, probably ester.
Run 3	Particulate Filter Catch	Aliphatic hydrocarbon with small amounts of aliphatic ester, anhydride and a third carbonyl containing compound. Significant aromaticity.
	Cyclone Catch	Very similar to the filter. There is much less aromaticity and slightly less ester.
	XAD-2	Benzoic acid, short chain carboxylic acid and a third carbonyl, probably ester.

TABLE 18. INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF COMBINED WASHES, RUN A

Fraction Number	Interpretation
1	Aliphatic hydrocarbon.
2	No material present.
3	Doubly conjugated ketone (similar to anthrone). Additional substitution on an aromatic ring indicates 2 adjacent hydrogens on the major aromatic. Evidence for aromatic amide.
4	Same as Fraction 3 with less indication for the aromatic amide.
5	Very similar to Fraction 4.
6	Doubly conjugated ketone (quinone possible) and/or carbamate.
7	Same as Fraction 6 with some isocyanate appearing.

TABLE 19. INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF XAD-2 EXTRACT, RUN A

Fraction #	Interpretation
1	Branched hydrocarbon.
2	Nothing detected.
3	Trace of hydrocarbon.
4	Small amount of ester of benzoic acid.
5	Trace of aromatic ester.
6	Benzoic acid.
7	Carboxylic acid salt.

TABLE 20. INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF COMBINED WASHES, RUN C

Fraction #	Interpretation
1	Aliphatic hydrocarbon.
2	Nothing detected.
3	Silicone and possibly a small amount of amide.
4	Aliphatic nitro compound and some carbonyl. Organic nitrate or nitrite is possible.
5	Same as Fraction 4.
6	Same as Fraction 4.
7	Inorganic nitrate.

TABLE 21. INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF XAD-2 EXTRACT, RUN C

Fraction #	Interpretation
1	Aliphatic hydrocarbon, branched.
2	Aliphatic hydrocarbon, branched.
3	Trace of aliphatic ester.
4	Aromatic ester, probably including benzoate.
5	Aromatic ester and acid.
6	Aromatic carboxylic acid.
7	Carboxylic acid salt.

TABLE 22. INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF COMBINED WASHES, RUN D

Fraction #	Interpretation
1	Aliphatic hydrocarbon with branching
2	Aliphatic hydrocarbon, small amount of ester.
3	Silicone with a small amount of aromatic.
4	Aliphatic hydrocarbon with low levels of a probable ester and possible amide.
5	Same as Fraction 4.
6	Isocyanate. Evidence for urethane.
7	Low levels of carboxylic acid salt.

TABLE 23. INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF XAD-2 EXTRACT, RUN D

Fraction #	Interpretation
1	Aliphatic hydrocarbon, branched.
2	Hydrocarbon, small amounts of ester and silicone.
3	Hydrocarbon and ester.
4	Hydrocarbon with ester, silicone and some aromaticity.
5	Ester, possible phthalate.
6	Benzoic acid.
7	Carboxylic acid salt.

TABLE 24. INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF COMBINED WASHES, RUN E

Fraction #	Interpretation
1	Aliphatic hydrocarbon with a trace of ester.
2	Hydrocarbon with low levels of ester and silicone.
3	Silicone, some aromatic, possibly unsaturated.
4	Hydrocarbon with a small amount of ester.
5	Hydrocarbon with a small amount of amide or urethane structure.
6	Urethane structure with a small amount of isocyanate.
7	Carboxylic acid salt with some inorganic nitrate.

TABLE 25. INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF XAD-2 EXTRACT, RUN E

Fraction #	Interpretation
1	Aliphatic hydrocarbon, some branching.
2	Aliphatic hydrocarbon with a small amount of ester.
3	Aromatic hydrocarbons. Both mono and meta substitutions are present indicating at least two compounds or a biphenyl.
4	Ester of benzoic acid, possibly ethylene glycol dibenzoate.
5	Ester of benzoic acid.
6	Benzoic acid.
7	Low levels of several carbonyls, ethers and carboxy salts.

TABLE 26 . INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF XAD-2 EXTRACT, RUN M

Fraction Number	Interpretation
1	Aliphatic hydrocarbon.
2	Traces of hydrocarbon.
3	Trace of benzoate.
4	Benzoate and an aromatic ester.
5	Benzoate, small amount of ketone and trace quantities of tricresyl phosphate.
6	Benzoic acid.
7	Carboxylic acid salt and some ester.

TABLE 27. INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF XAD-2 EXTRACT, RUN 0

Fraction Number	Interpretation
1	Branched aliphatic hydrocarbon with a very small amount of aromaticity.
2	Aliphatic and aromatic hydrocarbon.
3	Benzoate and aliphatic hydrocarbon.
4	Benzoate ester and small amount of amide.
5	Benzoate, aldehyde or ketone and traces of amide and tricresyl phosphate.
6	Benzoic acid.
7	Carboxylic acid salt.

TABLE 28. INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF XAD-2 EXTRACT, RUN S

Fraction Number	Interpretation
1	Aliphatic hydrocarbon.
2	Aliphatic and aromatic hydrocarbons.
3	Aromatic α,β-unsaturated ester, possibly benzoate. Some amide probable.
4	Aromatic ester, possibly benzoate. Amide probable.
5	Benzoate. Small amount of ketone and trace of tricresyl phosphate.
6	Benzoic acid.
7	Aromatic carboxylic acid salt, partly benzoic acid salt. Small amount of an ester.

TABLE 29. INFRARED SPECTROSCOPY RESULTS FOR LIQUID CHROMATOGRAPHY OF XAD-2 EXTRACT, RUN 1

Fraction Number	Interpretation
1	Aliphatic hydrocarbon with a small amount of aromatic and a trace of ester.
2	Aromatic hydrocarbon. Indications for fused rings and rings with 2 adjacent hydrogens.
3	Ester, benzoic acid and amide or carbonate.
4	Aliphatic hydrocarbon, small amount of ester and what is probably a nitrogen heteroaromatic, possibly a triazine.
5	Hydrocarbon and a trace of aliphatic ester.
6	Aliphatic carboxylic acid salt.
7	Carboxylic acid salt.

TABLE 30. INFRARED SPECTROSCOPY RESULTS FOR BLANK LIQUID CHROMATOGRAPHY

Fraction #	Interpretation
1	Nothing detected.
2	Nothing detected.
3	Nothing detected.
4	Low levels of aromatic amine and carbonyl. Could be similar to EDTA.
5	Nothing detected.
6	Trace of structure similar to Fraction 4.
7	Low levels of carboxylic acid salt, very short chain.

TABLE 31. LOW RESOLUTION MASS SPECTROMETRY RESULTS FOR SELECTED LIQUID CHROMATOGRAPHY FRACTIONS

Sample	Fraction #	Intensity	Intrepretation
Combined washes	2 and 3	100	Phthalates
Run A		5	Aromatic amine
		30	Carboxylate
	4	100	Phthalates
		20	Fused ring compounds
	5	100	Phthalates
		15	Fused ring compounds
	6 and 7	100	Phthalates
		10	Alcohol
XAD-2 extract	6 and 7	100	Carboxylates
Run A		25	Phthalates
		25	Amine
		20	Benzoic acid
Combined washes	6 and 7	100	Carboxylates
Run C		40	Methyl esters
		25	Phthalates
		15	Aromatic amines
XAD-2 extract	6 and 7	100	Carboxylates
Run C		30	Phthalates
		30	Benzoic acid
		15	Aromatic amines

TABLE 32. AAS ANALYSIS FOR MERCURY ON XAD-2 SORBENT CARTRIDGES

Sample I.D.	Mercury (μg/sample)
A79	21
B81	9.0
C80	95
D72	10
E329	400

TABLE 33. AAS ANALYSIS FOR MERCURY ON PARTICULATE FILTER CATCHES

Sample I.D.	Mercury µg/sample
A6	3.7
B8	28
C7	9.1
D7	180
E7	7.6
M7	3.1
O7	2.2
R7	15
S7	2.6
1-7	5.1
2-7	0.6
3-7	11

TABLE 34. AAS ANALYSIS FOR MERCURY IN $>3\ \mu m$ PARTICULATE CYCLONES

Sample I.D.	Mercury µg/sample
B7	24
C8	17
D8	220
E8	34
M8	6.1
O8	16
R8	20
S8	66
1-8	56
2-8	<20
3-8	76

TABLE 35. AAS ANALYSIS FOR MERCURY ON ORGANIC RINSE AND EXTRACTED CONDENSATE

Sample I.D.	Mercury (μg/sample)
A4	5.2
B4	0.8
C4	<0.1
D4	0.5
E4	1.8

TABLE 36. AAS ANALYSIS FOR MERCURY ON FIRST IMPINGER SOLUTIONS

Sample I.D.	Mercury µg/sample
A3	5.3
B1	0.7
C1	5.5
D1	1.4
E1	4.3
M1	3.5
O1	2.8
R1	0.7
S1	2.0
1-1	0.7
2-1	0.5
3-1	0.8

TABLE 37. AAS ANALYSIS FOR MERCURY, ARSENIC, AND ANTIMONY ON SECOND AND THIRD IMPINGER SOLUTIONS (COMBINED)

Sample I.D.	Mercury µg/sample	Arsenic µg/sample	Antimony µg/sample
A2	5.7	0.6	<10
B2	0.1	<0.4	<10
C2	13	1.3	<10
D2	0.2	2.0	<10
E2	0.6	2.9	<10
M2	16	<0.4	<10
O2	6.5	<0.4	<10
R2	4.0	<0.4	<5
S2	<0.7	<0.4	<10
1-2	3.0	<0.4	<10
2-2	1.1	1.2	<10
3-2	1.3	<0.4	<10

TABLE 38. RESULTS OF PAH SPOT TESTS ON PARTICULATE FILTER EXTRACTS

Sample I.D.	POM Concentration (g/l)
A6	$<10^{-6}$
B8	$<10^{-6}$
C7	$<10^{-6}$
D7	$<10^{-6}$
E7	$<10^{-6}$
M7	$<10^{-6}$
07	$<10^{-6}$
R7	$<10^{-6}$
S7	$<10^{-6}$
1-7	10^{-3}
2-7	$<10^{-6}$
3-7	10^{-3}

TABLE 39. PAH ANALYSIS OF XAD-2 EXTRACTS OF SELECTED RUNS

Compound (µg/sample)	Run I. D.			
	1	3	S	0
Naphthalene	4	2	<0.5	0.5
Acenaphthene	3	<0.5	<0.5	<0.5
Phenanthrene	<0.5	3	<0.5	<0.5
Fluoranthene	3	<0.5	<0.5	<0.5
Chrysene	3	8	<0.5	<0.5
Benzofluoranthene	15	24	<0.5	<0.5
Benzo(e)pyrene	0.7	2	<0.5	<0.5
Indeno(1,2,3-c,d)pyrene	2	8	<0.5	<0.5
Benzo(g,h,i)pyrene	14	<0.5	<0.5	<0.5
Coronene	16	13	<0.5	<0.5

Detection Limit 0.5 µg

TABLE 40. GAS CHROMATOGRAPHY ANALYSIS FOR ORGANIC CHLORINE ON COMBINED WASHES

Sample I.D.	Organic Chlorine ($\mu g/m^3$)
B3/B4/B5/B6	12
D3/D4/D5/D6	13
E3/E4/E5/E6	26
03/04/05/06	5
S3/S4/S5/S6	0.7
1-3/1-5/1-6	1

TABLE 41. GAS CHROMATOGRAPHY ANALYSIS FOR ORGANIC CHLORINE ON XAD-2 EXTRACTS

Sample I.D.	Organic Chlorine ($\mu g/m^3$)
A79	5
B81	5
D72	27
E329	34
M9	6
O9	9
R9	5
S9	5
1-9	7
2-9	6
3-9	4

TABLE 42. GAS CHROMATOGRAPHY ANALYSIS FOR ORGANIC CHLORINE ON PARTICULATE FILTER EXTRACTS

Sample I.D.	Organic Chlorine ($\mu g/m^3$)
A6	ND
B8	ND
D7	ND
E7	ND
M7	ND
07	ND
R7	ND
S7	ND
1-7	ND
2-7	ND
3-7	ND

ND = not detected.

TABLE 43. GAS CHROMATOGRAPHY ANALYSIS FOR ORGANIC CHLORINE ON CYCLONE CATCH EXTRACTS

Sample I.D.	Organic Chlorine ($\mu g/m^3$)
B7	ND
D8	0.1
E8	ND
M8	0.1
O8	ND
R8	ND
S8	ND
1-8	0.6
2-8	ND
3-8	ND

TABLE 44. RESULTS OF HRGC/HRMS ANALYSES FOR 2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN IN XAD-2 EXTRACTS

Sample	Amount of TCDD Present in Sample, ng	% Recovery of ^{13}C-Labeled TCDD Internal Standard
Run 0	<2.0	97
Run 1	<3.1	40
Run 5	<1.5	65

TABLE 45. SAMPLES CONTAINING TRACE LEVELS OF TETRACHLOROBIPHENYL (Tentative)

Sample I.D.
B3/B4/B5/B6
D3/D4/D5/D6
D72
E3/E4/E5/E6
E8
E329
03/04/05/06
0-9
R-9
S-9
1-9
3-9

TABLE 46. AAS ANALYSIS FOR MERCURY, ARSENIC AND ANTIMONY OF FUEL SAMPLES

Sample I.D.	Mercury (μg/g)	Arsenic (μg/g)	Antimony (μg/g)
Coal	0.05	4.6	<2.0
Refuse Derived Fuel	0.31	1.0	<2.0